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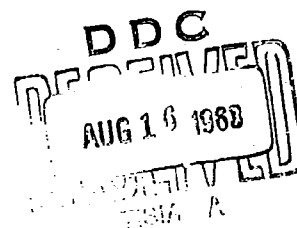
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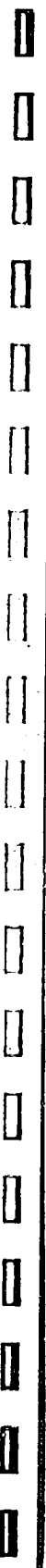
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ENVIRONMENTAL CONTROL SYSTEMS

FOR

CLOSED UNDERGROUND SHELTERS

Contract No. OCD-OS-62-56

Prepared by

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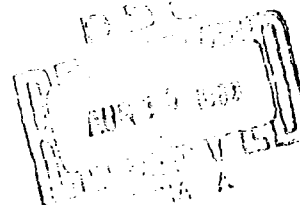
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ABSTRACT

        This report summarizes the results of a study to determine the most practical
and economical methods for controlling oxygen, carbon dioxide, odors, trace gases,
and temperature-humidity in a closed underground shelter. The maximum time which
the shelter would be sealed because of the presence of external fires or chemical
and biological warfare agents was designated as 24 hours. An extensive literature
and industrial survey of all types of feasible environmental control systems was
supplemented by experimental studies.

        From a standpoint of cost, safety, reliability, and ease of handling the
following systems are recommended:

        1.   Oxygen Supply - Breathing oxygen should be supplied by high pressure
gas cylinders equipped with a regulator and small flowmeter.

        2.   Carbon Dioxide Removal - Lithium hydroxide, Baralyme, and soda-lime
are best suited for controlling the concentration of carbon dioxide within a
fallout shelter. As an extreme minimal survival method lithium hydroxide may
be employed in a static or passive system; however, the use of Baralyme or soda-
lime in a manual powered blower-canister system is recommended.

        3.   Odor and Trace Gas Removal - Certain undesirable gases may be produced
by human metabolism (passing flatus) or activities (smoking). Activated carbon
will remove most higher molecular weight contaminants but catalytic combustion
devices would be required if gases such as carbon monoxide and methane are to be
removed.

        4.   Temperature-Humidity Control - The optimal method of temperature-humidity
control in an underground shelter depends upon the particular shelter in question.
Temperature and humidity control systems, if required, should be custom designed
to each shelter or type of shelter.

SUMMARY

Contract OCD-OS-62-56 (Project 1107) was initiated in March 1962 and was completed in April 1963. The project entailed the investigation and cost analyses of atmosphere control techniques for use in closed underground fallout shelters. Internally located, self-contained environmental control systems are required for shelter atmosphere contol whenever the presence of nearby outside fires precludes the supply of outside air to the shelter. Environmental control systems which were evaluated included all conceivable types of oxygen supply, carbon dioxide and toxic constituent removal, and temperature and humidity control. The project was divided into four principal categories as follows: (1) study of man's physiological environmental requirements, (2) engineering evaluation and analysis of all conceivable systems, (3) experimental investigations of candidate systems, (4) application study for selection of the appropriate system for particular shelter types.

1. Environmental Requirements

An extensive literature study was conducted to determine human tolerance to variations in certain environmental parameters. Oxygen content should ideally be maintained at 20 per cent; however, 12 per cent will sustain human life, allowing for a decrement in performance and capabilities. Similarly, carbon dioxide content should ideally be controlled to less than one per cent, whereas concentrations as high as 4 per cent may be tolerated at the expense of lower performance ability and higher oxygen consumption rates. For purposes of this study, oxygen consumption was assumed to be one cubic foot per hour and carbon dioxide production rate 0.85 cubic foot per hour for each person in the shelter. An effective temperature of 72°F is ideal but 85°F was established as the tolerance limit.

2. Engineering Evaluation

The engineering evaluation was divided into four phases as indicated below:

Oxygen Supply - Methods which were evaluated include both chemical and mechanical storage, and the chemical recovery of oxygen from carbon dioxide. Examples of the latter method are the use of green plants such as algae to effect photosynthetic recovery, or the hydrogenation of carbon dioxide to form water which is subsequently electrolyzed to produce respiratory oxygen. Chemical storage methods utilize compounds such as hydrogen peroxide, calcium peroxide, potassium superoxide, sodium superoxide, chlorate candles, and salcomine. Mechanical storage of oxygen in both the liquid and gaseous forms were evaluated.

From a standpoint of safety, reliability, and ease of handling it was found that breathing oxygen should be supplied by either chlorate candles or high pressure gas cylinders equipped with a regulator and a small flowmeter. Since the gas cylinder method is less expensive than the use of chlorate candles the former method is recommended unless the shelter is a very small one occupied by less than five persons.

Carbon Dioxide Removal - Methods which were evaluated include: (1) Solid Adsorbents such as Molecular Sieves and activated carbon; (2) Solid Absorbents such as anhydrous lithium hydroxide, silver oxide, soda-lime, Baralyme, sodium and potassium superoxide; (3) Liquid Absorbents such as alkali hydroxide solutions, alkali earth hydroxides, alkali carbonates, ethanolamines, Alkazid M, sulfates, and water; (4) Mechanical Techniques such as freeze-out and diffusion methods.

These studies showed that three solid absorbents; namely, lithium hydroxide, Baralyme, and soda-lime are best suited for controlling the concentration of carbon dioxide within a closed fallout shelter. The anhydrous lithium hydroxide has been nationally advertized as a material to control carbon dioxide in shelters under the trade name, Granlox. All three absorbents were tested during the experimental phase of this project.

Toxic Trace Gas Control - These gases may arise from human metabolism (passing flatus) or certain activities (smoking). The engineering evaluation indicated that activated carbon will remove most higher molecular weight contaminants. For control of gases such as methane or carbon monoxide catalytic combustion or Hopcalite units are required.

Temperature-Humidity Control - All types of methods were considered including passive techniques such as thermal bus bars, chemical methods employing desiccants, use of proximate well water, and mechanical refrigeration techniques such as vapor compression systems, absorption systems, and air cycle systems. The optimal method for temperature-humidity control in a fallout shelter depends upon the particular conditions experienced at each shelter. For instance, if well water were available for cooling then a desiccant could be employed for humidity control. The use of a desiccant alone, however, would increase the effective temperature even though the relative humidity were decreased. Conversely, the use of well water alone would limit the minimum dew point which could be obtained.

3. Experimental Investigations

The engineering analyses indicated the theoretical superiority of lithium hydroxide, Baralyme and soda-lime over other types of carbon dioxide removal techniques. However, the literature and industrial survey failed to uncover sufficient experimentally determined performance data upon which application specifications could be based. The experimental phase of the project, therefore, was concerned with evaluating the practical effectiveness of the following carbon dioxide removal methods:

(a) Use of anhydrous lithium hydroxide crystals employing static or passive techniques.

(b) Use of either soda-lime or Baralyme in canisters in dynamic (blower) systems.

The tests indicated that: (1) the lithium hydroxide crystals (Granlox) possessed an excessive tendency to dust and that the performance capabilities of static absorption techniques were impossible to predict accurately; (2) the use of Baralyme and soda-lime in canisters was entirely satisfactory. In addition, these experiments provided information which was used to obtain preliminary optimization data for dynamic carbon dioxide absorption systems.

4. Results and Conclusions

Development of convenient and inexpensive dispensing and manifolding equipment for oxygen cylinders is required. The presently available equipment is not only too expensive but too complicated for use by the average citizen, especially during periods of high emotional stress.

The passive or static use of any carbon dioxide absorbent is not recommended, except as an extreme minimal survival measure, because of the difficulty of assuring the adequate performance of this method. Lithium hydroxide could be used in a dynamic (blower-canister) system but both soda-lime and Baralyme are less expensive. Therefore, the use of soda-lime or Baralyme in hand-powered, blower-canister systems is advocated for carbon dioxide absorption in closed shelters. Further design data is required in order to accurately size dynamic systems (or static systems if cost prohibits the use of dynamic systems). This data must be obtained by prototype fabrication, test, and redesign.

Temperature and humidity control techniques, if required, should be custom designed to the particular shelter or type of shelter in question. An experimental investigation on the adaptability of air cycle refrigeration systems to fallout shelters is highly recommended. Air cycle systems may be particularly well suited for use in fallout shelters because of their high intrinsic reliability after long periods of infrequent use, and freedom from the possibility of refrigerant leakage.

The chart on the next page is a synopsis of all available relevant costs for providing various degrees of environmental control for fallout shelters. As shown, the total per person cost varies with the type of components and materials selected and with the size of the shelter. Per person costs are, in general, lower for larger shelters and higher for smaller shelters because of quantity purchase discounts and more favorable distribution of fixed costs.

SUMMARY OF PER PERSON COSTS FOR 24 HOURS

	10-Man	100-Man	1000-Man
Oxygen			
Chlorate Candles	$16.00	$12.00	$12.00
Cylinder, gas, and flowmeter	8.45	5.00	4.23
CO_2 Removal			
Anhydrous Lithium Hydroxide	$14.00	$12.00	$12.00
Baralyme or Soda-Lime	3.80	3.80	3.80
With Centrifugal Hand Blower	6.80	5.80	5.50
With Positive Displ. Hand Blower	8.80	8.80	8.50
Additional Cost for Electrical Motor	*	10.00	10.00
Trace Gas Removal			
Activated Carbon	$ 0.35	$ 0.35	$ 0.35
Catalytic Burner	*	6.00	4.50
Hopcalite	*	**	**
Temperature-Humidity Control			
Well Water	**	**	**
Desiccant	$ 0.32	$ 0.32	*
Vapor Compression System	*	12.00	$10.00
Air Cycle System	**	**	**

*   Not Recommended
** Information Presently Unavailable.

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SECTION 1

INTRODUCTION

1.1 Background

During World War II large numbers of people lost their lives in bombing attacks due to the effects of mass fires, even though they were seemingly protected in air raid shelters. Even before the introduction of atomic weapons at the end of the war, mass fires were a frequent cause of death during bombings. A good example of this was the mass fire created in Tokyo on March 9, 1945 which destroyed an area of 16 square miles and caused more than 80,000 deaths and more than 100,000 injuries, perhaps more than in Hiroshima and Nagasaki combined. (Ref. 1)* In a fire raid on Hamburg on July 27, 1943, two-thirds of all the buildings within a 5 square-mile area were ablaze within 20 minutes. Within a few hours the fire had begun to run out of fuel and die down - although the hot rubble heaps made large areas unapproachable for several days. (Ref. 2)

The greatest number of deaths in these areas occurred in basements or makeshift shelters. Since the position of the corpses indicated that death came peacefully and unexpectedly the cause of death has been attributed to one or more of the following reasons:

1. Carbon monoxide poisoning resulting from large amounts of the lethal gas created by the fires being drawn into the shelters.

2. Asphyxiation resulting from the depletion of oxygen either through conversion to carbon dioxide or by suction created within the burning area.

3. The effects of inhaling hot blasts of air drawn in by the shelter ventilation system.

4. Roasting of the shelter occupants as a result of conductive heat transfer into the shelter.

Although much of the evidence of cause of death in wartime shelters is ambiguous it is known that mass fires may very well create large amounts of carbon monoxide in the area. Very small amounts of this gas are lethal (see Section 2.1) and may be present in the fire area for long periods of time, especially if smouldering rubbles exist.

It is doubtful that the amount of combustible material present would consume quantities of oxygen of significant proportion to cause a dangerous or even noticeable decrease in oxygen content of ambient air. Also, tests have failed to indicate anything but a slight drop in pressure due to mass fires.

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* A list of references is found at the end of the report.

The heat created by mass fires is a dangerous factor to inhabitants of underground shelters only by way of the ventilation system. As little as three feet of surrounding earth reduces the heat transfer from external fires to the shelter environment such that any temperature rise in the shelter environment is negligible unless the fires persist for unusually long periods. Direct intake of hot "ventilating" air into the shelter could be a direct cause of death to the shelter inhabitants.

In view of the foregoing it becomes obvious that the most expeditious means of protecting the inhabitants of an underground shelter from the effects of external mass fires is the shut-down of the ventilation system and closure of the intake. An alternate to complete closure is the intake of external air from a remote location which happens to be reasonably cool and free of dangerous gases. Closure may also be required to protect against biological and chemical warfare.

This closure creates internal environmental hazards which must be eliminated by special internal equipment. These dangers and the operating requirements for the environmental control equipment are described in the next section.

1.2 Program Objectives

The objectives of the program were to determine the optimum method for controlling the internal environment of a sealed underground shelter; either by the incorporation of self-contained environmental control systems, or by the intake of safe air from some remote location. The environmental control system(s) recommended must be economical, safe, reliable, simple to use, and require minimal, if any, power. The system capabilities must include the provision of breathing oxygen, the removal of carbon dioxide and other harmful gases, and (in certain cases) the control of temperature-humidity. The maximum duration of operation for the system(s) was designated as 24 hours.

The program was divided into three phases; namely, an engineering analysis phase, experimental evaluation phase, and an application study phase.

1.2.1 Engineering Analysis Phase

This phase consisted of a comprehensive review and survey of all environmental control systems which could be applied to sealed shelters. The analysis compared the practicality, present cost, and availability of each system. Also investigated in this phase was the present capability of industrial production facilities to produce the required equipment and chemicals. This information was employed in determining whether or not extensive expansion of modernization of production facilities would be required.

The engineering analysis included a study of power requirements for each candidate system. Also determined was whether modifications would reduce or eliminate the need for power. An energy balance of candidate systems was made to determine the amount of waste heat generated and its effect on the shelter environment.

The weight and volume requirements of promising systems were ascertained to indicate if modifications could be made without decreasing effectiveness and maintainability and without increasing the cost.

The candidate systems were evaluated for ease of maintenance, safety, ease of repair, shelf life and overall reliability.

Suggestions for improvements in the above categories were also made.

1.2.2 Experimental Study Phase

During the literature survey it was found that information concerning the performance characteristics of several carbon dioxide absorbents was lacking. Therefore, the experimental study phase was concerned with obtaining sufficient performance data upon which preliminary designs of the recommended systems could be based. This information was then incorporated in the application phase.

1.2.3 Application Study

With the completion of the engineering analysis and experimental phases, the data obtained was correlated and reduced to determine the best present system or systems for 10-, 100-, and 1000-man shelters. In each category, the cost, volume and power requirements were deduced on a per person basis. Schematics of these systems are also included and recommendations are made for improvement of present system components and equipment.

SECTION 2

ENGINEERING ANALYSIS

2.1 Environmental Requirements

To sustain human life over an extended period of time* within the confines of a sealed shelter certain internal environmental parameters must be controlled between the limits of physiological tolerance. These parameters include the following: (1) oxygen content, (2) carbon dioxide content, (3) level of odiferous or toxic trace gases, (4) temperature-humidity. This section stipulates the physiological tolerable levels of these factors, and the rates at which human metabolism changes these parameters.

2.1.1 Oxygen and Carbon Dioxide

During normal breathing a man utilizes about 15 per cent of the vital capacity of his lungs during each respiration. Also, man's rate of respiration may be increased over his resting rate of approximately 17 (or less) respirations per minute by a factor of four. Thus, man's lung ventilation flowrate may be increased by an overall factor of as much as 25 in times of physical or emotional stress. (Ref. 3)

In normal individuals there exists a fairly constant difference between the percentage of oxygen concentration of inspired air to that of expired air. This value is termed the oxygen utilization coefficient and varies from 4.6 per cent, at rest, and may be increased by about 0.5 per cent in moderate exercise. (Ref. 4). It is a measure of the oxygen actually transferred by the alveoli to the blood stream for the subsequent oxidation of various materials in the body.

As the oxidation occurs during body metabolism the body tissues, in turn, produce a quantity of carbon dioxide. Venous blood contains more carbon dioxide but less oxygen than arterial blood. In its passage through the lungs, oxygen goes into the blood and carbon dioxide passes out of solution. The ratio of the volumes, CO_2-O_2 which are exchanged in a given time, is called the respiratory quotient, and is normally equal to approximately 0.85. (Ref. 5) This ratio varies according to the nature of the materials subjected to metabolic combustion in the body and to other conditions.

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* The length of time during which closure will be required is impossible to predict. All calculations in this report relating to closure are based on an estimate of 24 hours.

The listing below gives a rough average of the concentrations of oxygen, nitrogen, and carbon dioxide in inspired and expired air. (Ref. 6) The relative volume of nitrogen is slightly greater in expired air due to the removal of a certain amount of oxygen, without a proportionate increase in the production of carbon dioxide. In this table, the oxygen utilization coefficient is calculated as 4.55 per cent, and the respiratory quotient is 4.06/4.55 equal to 0.89.

	Inspired Air	Expired Air
O_2	20.95%	16.4%
N_2	79.01%	79.5%
CO_2	0.04%	4.1%

On a mass basis, the amount of oxygen utilized by man doing light work during a 24-hour period is approximately 2 lbs, although this value may vary greatly dependent upon breathing volume and rate. On a volume basis, assuming 17 respirations per minute, 30.5 cubic inches inspired per respiration, and an oxygen utilization coefficient of 5 per cent, approximately 0.9 cubic feet of oxygen are consumed per hour (STP). Assuming a respiratory quotient of 0.85, approximately 2.3 lbs of carbon dioxide would be produced in one day or 0.76 cubic feet per hour (STP).

Depending upon the shelter volume per inhabitant, the oxygen content decreases and the carbon dioxide content increases with time as shown by Figure 1. (Ref. 7)

Reduced oxygen content in inspired air results in a lack of oxygen in the body known as hypoxia. The effects of increasing degrees of hypoxia are listed in Table 1. (Ref. 8) The physiological effects of increasing amounts of carbon dioxide in inspired air are listed in Table 2. (Ref. 9). These tables and Figure 1 show that carbon dioxide content approaches physiologically dangerous levels at a faster rate than does oxygen.

It is noted that increased carbon dioxide tension in the blood reduces the oxygen-retaining power of the hemoglobin and also is the determining factor in controlling the depth and rate of respiration. The respiratory center is sensitive to an increase of 0.2 per cent in carbon dioxide content of inspired air. The lung action is doubled when inspired air contains 3 per cent carbon dioxide. Oxygen content on the other hand can be drastically reduced without affecting the depth or rate of respiration. For this reason, hypoxia is a more insidious danger than carbon dioxide narcosis.

Figure 1 CARBON DIOXIDE AND OXYGEN IN OCCUPIED SPACES

TABLE 1   EFFECTS OF OXYGEN DEFICIENCY

Oxygen Content of Inhaled Air, Per cent	Effects
20.9	No effects; normal air
15	No immediate effects
10	Dizziness; shortness of breath; deeper and more rapid respiration; quickened pulse, especially on exertion
7	Stupor sets in
5	Minimal concentration compatible with life
2-3	Death within a few minutes

TABLE 2   EFFECTS OF CARBON DIOXIDE - OXYGEN CONTENT NORMAL

Carbon Dioxide Content of Inhaled Air, Per cent	Effects
.04	No effects; normal air
2.0	Breathing deeper; air inspired per breath increased 30 per cent
4.0	Breathing much deeper; rate slightly quickened; considerable discomfort
4.5-5	Breathing extremely labored; almost unbearable for many individuals; nausea may occur
7-9	Limit of tolerance
10-11	Inability to coordinate; unconsciousness in about ten minutes
15-20	Symptoms increase, but probably not fatal in one hour
25-30	Diminished respiration; fallout of blood pressure; coma; loss of reflexes; anesthesia; gradual death after some hours

2.1.2 Odor and Toxic Gases

The most imminent danger to shelter occupants from surface fires is carbon monoxide poisoning. It is rapidly effective since it combines with hemoglobin forming CO-hemoglobin and its affinity to combine is 300 times as great as oxygen. The blood is therefore deprived of its oxygen carrier and the person dies of asphyxia. Table 3 shows the effects of various concentrations of carbon monoxide in the shelter environment. (Ref. 10) However, if ideal functioning of the ventilation sealing system can be assumed, the major source of carbon monoxide is eliminated. Section 2.3.1, Odor and Contaminant Control, includes a list of maximum allowable concentrations of various other gases which could be encountered in shelters.

TABLE 3

EFFECTS OF CARBON MONOXIDE

Carbon Monoxide Content of Inhaled Air, Per cent	Effects
0.02	Possible mild frontal headache after three hours
0.04	Frontal headache and nausea after one to two hours; occipital (rear of head) headache after two and one-half to three and one-half hours
0.08	Headache, dizziness, and nausea in forty-five minutes; collapse and possible unconsciousness in two hours
0.16	Headache, dizziness, and nausea in twenty minutes; collapse, unconsciousness and possible death in two hours
0.32	Headache and dizziness in five to ten minutes; unconsciousness and danger of death in thirty minutes
0.64	Headache and dizziness in one or two minutes; unconsciousness and danger of death in ten to fifteen minutes
1.28	Immediate effect; unconsciousness and danger of death in one to three minutes

2.1.3 Temperature and Humidity

Sources of heat within an underground fallout shelter include the following:

1. Metabolic heat from the inhabitants.

2. Heats of reaction from chemicals used for oxygen supply, carbon dioxide absorption, desiccation, and trace gas removal.

3. Heat loss from internal equipment such as motors, lights, food warmers, etc.

The total rate at which heat is generated in the shelter environment from these sources is largely dependent upon or proportional to the total number of inhabitants occupying the particular shelter.

Human health and efficiency depend greatly on the body's ability to dissipate metabolic heat. To reject heat to the proximate environment the body utilizes the heat transfer modes of convection, conduction, radiation, and evaporation. Metabolic heat which is not rejected must be stored and reflected by a change in body temperature. These relationships may be expressed by the mathematical model,

$$\pm Q_S = Q_M + Q_E \pm Q_R \pm Q_C$$

As shown, stored heat may be either positive or negative, depending upon whether body temperature is increasing or decreasing; metabolic heat is always being produced; evaporative heat is usually positive, because body surface temperature is usually higher than the air dew point temperature; radiative heat transfer may be positive, or negative depending upon the surface temperature of the shelter walls and proximate objects; convective heat transfer may be positive or negative, depending upon whether the body surface temperature is higher than or lower than air dry bulb temperature. (Ref. 11)

Under normal conditions (sedentary activity, wall and air temperature of 70°F - 5°F, relative humidity of 50 per cent - 10 per cent, air movement of 25 fpm) deep body temperature remains relatively constant at approximately 98.6°F and 400 Btu/hr of metabolic heat is rejected to the proximate environment. (Ref. 12) Since body surface temperature under these conditions is about 85°F most of the metabolic heat (about 300 Btu/hr) can be rejected by convection. The remaining 100 Btu/hr is accounted for by the evaporation of about 0.1 lb/hr of water from the skin and lungs (insensible perspiration). (Ref. 13) If exposed to lower air temperatures the body will attempt to preserve the internal temperature and this attempt is reflected in increased convective heat losses (about 500 Btu/hr at 50°F). Evaporative heat losses due to insensible perspiration remain the same. If air temperature is increased the convective heat rejection must unavoidably decrease. The body then begins to utilize the powerful evaporative heat rejection method of sensible perspiration. At 95°F, for instance,

convective heat losses are about 50 Btu/hr and evaporative heat losses are about 350 Btu/hr. Figure 2 presents these relationships graphically, (Ref. 14) for the average person. These data are, of course, subject to wide variations with respect to size, weight, diet, activity, amount of clothing, etc.

Combinations of temperature and humidity can be tolerated for various times of exposure as shown in Figure 3. The shaded area indicates that certain appropriate combinations of temperature and relative humidity ranging from 57 to 94°F and 10 to 100 per cent can be tolerated indefinitely. (Ref. 15)

Table 4 presents a summarization of the latest studies related to the effects of extremes in temperature and humidity on human subjects in shelter conditions. (Ref. 16)

There are many common substances which, although not harmful in ordinary use, become potential dangers in nonventilated spaces. Cleaning agents, solvents, degreasers and dangerous refrigerants such as carbon dioxide should be eliminated. Such items as ammonia solution cleaner, pressurized shaving cream and similarly activated dispensers, mercury thermometers, cigarette smoke, and carbon dioxide fire extinguishers are very subtle hazards. (Ref. 16)

Certain odors are probably more psychologically harmful than physiologically. Perspiration, wastes, and other human metabolism products are important members of this group. Cooking and food decomposition odors would be distressing after extended exposure.

TABLE 4

ACCEPTABLE, AND TOLERABLE THERMAL LIMITS FOR
HEALTHY PEOPLE AT REST PROPERLY CLOTHED

Limits expressed in terms of Effective Temperature (E.T.), which is the temperature of saturated air with minimum air movement		
Lowest temperature endurable in cold weather for at least two weeks in emergencies	35°	E.T.
Possible Chilblain, or shelterfoot	35-50	"
Lowest acceptable for continuous exposure Manual dexterity may be affected	50	"
"Optimum" for comfort, with 60% relative humidity	68-72	"
Perspiration threshold. Acceptable for continuous exposure	78	"
Endurable in emergencies for at least two weeks. Possible heat rash in prolonged exposures	85	"
Possible heat exhaustion in unacclimatized people	88	"
Possible heat exhaustion in acclimatized persons	92	"

$$\pm Q_S = Q_M + Q_E \pm Q_R + Q_C$$
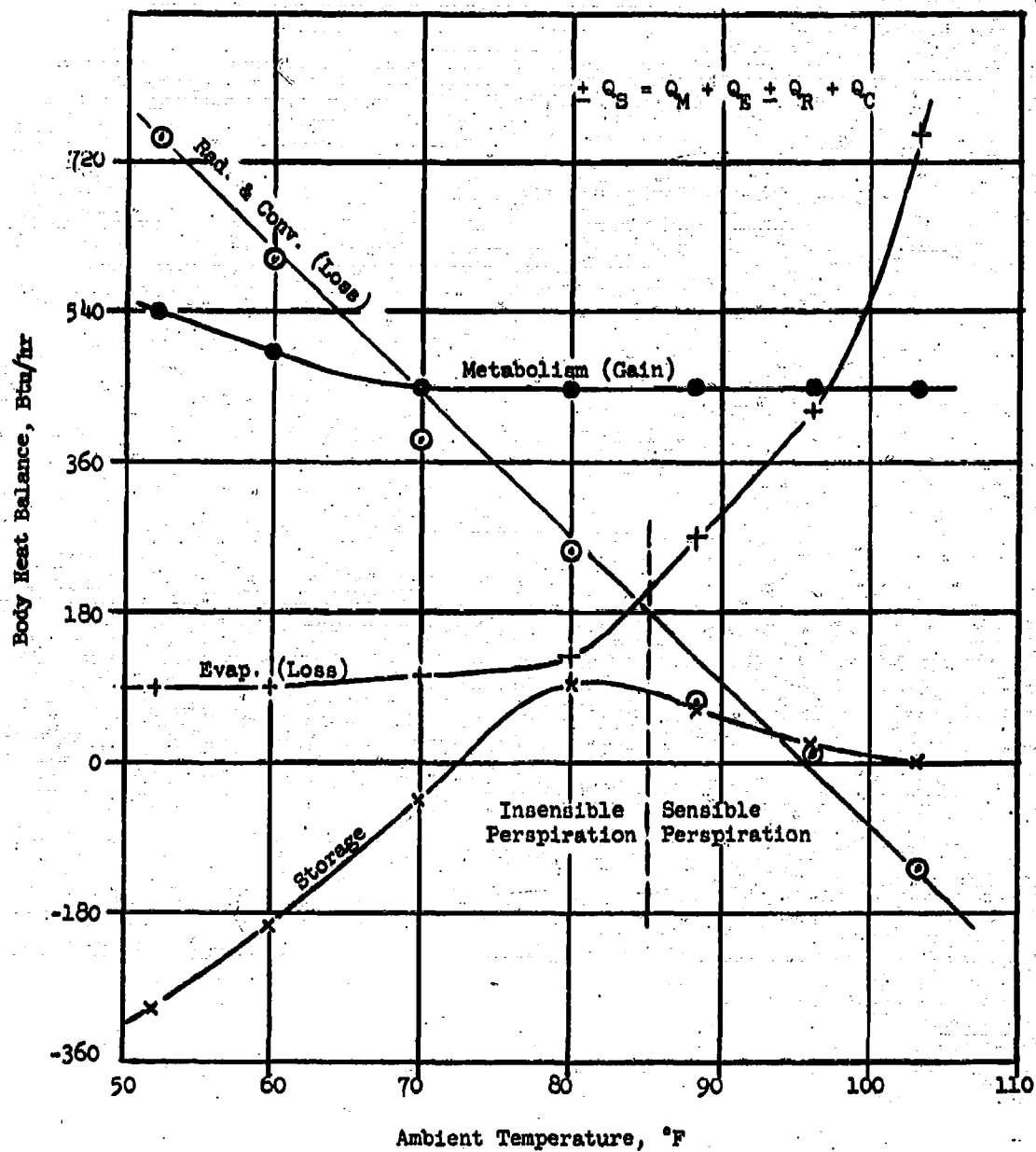
Figure 2   THERMAL INTERCHANGE
(CLOTHED SUBJECTS)

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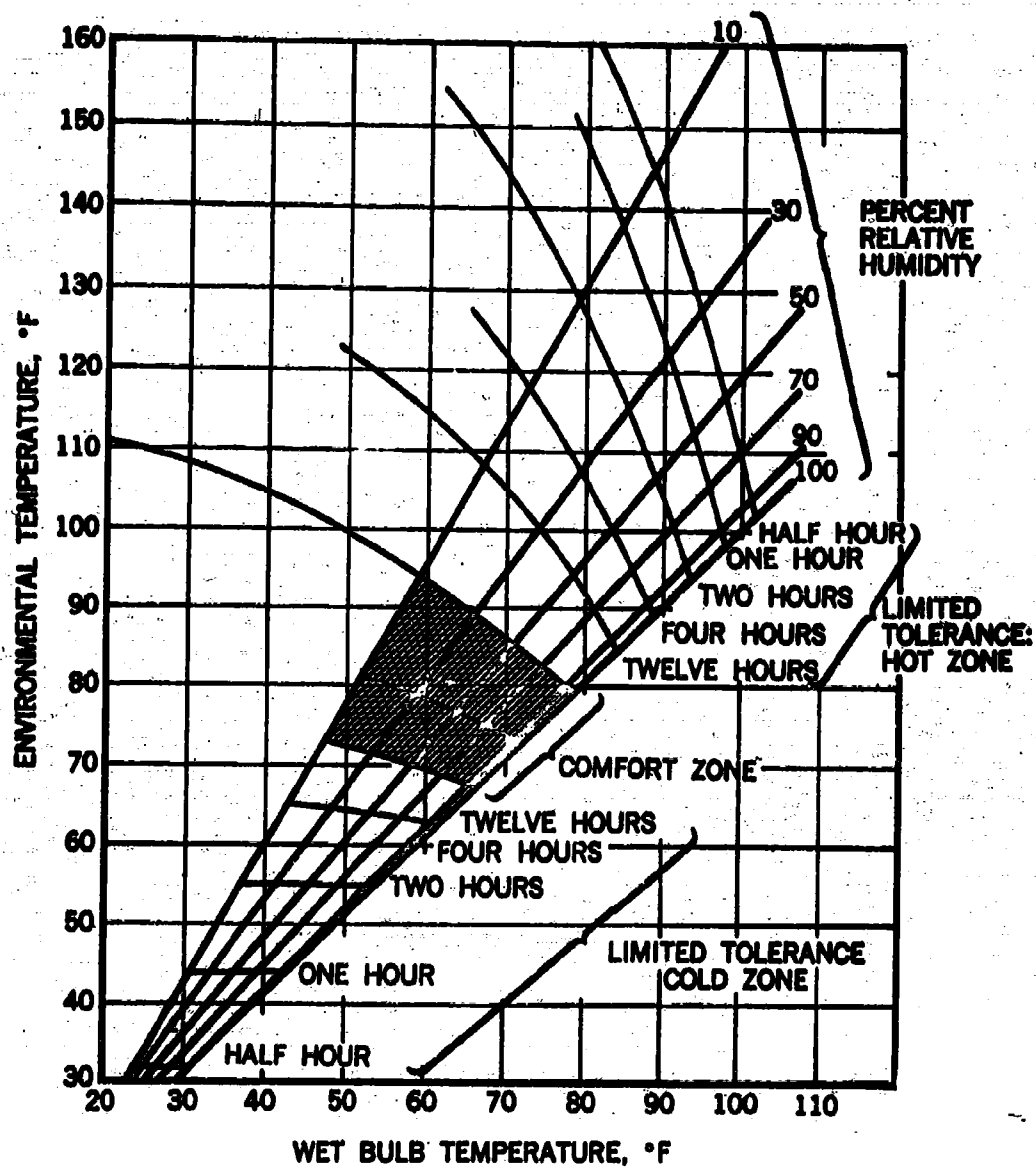
Figure 3 THERMAL REQUIREMENTS FOR TOLERANCE AND COMFORT
(PSYCHOMETRIC PLOT)

2.2 Oxygen Supply

Oxygen can be supplied to a sealed environment by releasing it from bulk storage or decomposing oxygen-rich chemicals. Bulk oxygen is contained either in high pressure cylinders or in the liquid state. These are considered as mechanical methods since no chemical reaction is involved. Chemical methods include decomposition by reaction, heating, or electrolysis.

2.2.1 Mechanical Methods

2.2.1.1 High Pressure Storage - Oxygen may be stored in steel or Fiberglas containers. These may be obtained in various sizes and pressure ratings. The advantage of higher pressures is high density storage and thus a smaller storage volume. The present high cost of Fiberglas cylinders eliminates them from further consideration for shelter.

Steel cylinders can be obtained for 10,000-psi service; however, the commercial gas cylinders are pressurized to 2400 psi. Special size cylinders are available from high pressure vessel manufacturers. The common commercial size contains 244-250 cubic feet (STP) of gas which is used to supply oxygen for medical and industrial applications.

Table 5 is a list of readily obtainable oxygen cylinders. These prices and sizes are based on data from the Matheson Company. Similar cylinders are available from other compressed gas firms. Normally the cylinder charge is a deposit which is fully refunded if the cylinder is returned within 30 days. However these cylinders will be stored for an indefinite period of time so they will have to be purchased by the oxygen consumer.

TABLE 5

OXYGEN CYLINDER DATA (Ref. 17)

Matheson Cylinder Size	Pressure (psi)	Gas Cost	Cylinder Charge	Total Cost	Vol. ft^3 (STP)	Gross wt. (lbs)	Dimensions	Man-hrs Supply
1A	2000	$6.00	$44.00	$50.00	244	151	9"dia x 52"	244
2	1600	4.90	35.00	39.90	70	73	8" x 27"	70
3	1600	3.65	26.00	29.65	28	32	6" x 21"	28
4	1600	3.10	21.00	24.10	10	16	4" x 14"	10
LB	1600	1.00	7.00	8.00	2	4	2" x 15"	2

The cylinders can be purchased directly from a steel fabricator. Below are listed the prices of a typical cylinder manufacturer, Harrisburg Steel Company.

Size Capacity (STP)	Price (100-299 cylinders)
220 cubic feet	$ 34.85
300	42.15
400	63.35
1500	224.00 (1 cylinder)
1770	262.00 (1 cylinder)

These cylinder prices include the collar and cap. The valve is an extra $2.85.

There is little cost difference if the gas is supplied from a few large cylinders or several smaller ones. The small cylinders have the advantage of ease of handling whereas one or two large cylinders would not need a manifold and offer a space savings. The final decision will probably be based on the shelter design.

A manifold, regulator, and flow meter assembly are recommended to control the flow rate of oxygen although in an emergency the cylinders can be opened without a regulator attached to them.

The principal hazard involved in the use of high pressure oxygen is that if a cylinder is knocked down the valve may be broken off and the cylinder will become self-propelled. If the cylinder is properly secured, there are no hazards involved in opening the valve and letting the oxygen into the air, however, combustible materials such as lubricants should not be stored near the delivery system.

2.2.1.2 Liquid Oxygen Storage - Oxygen may be stored in the liquid state. The liquid system has the advantage of storing large quantities of oxygen in a small volume because the liquid has a density of 71 pounds/ft3 at -297°F. (Ref. 18) Oxygen gas which is compressed to 2000 psi has a density of approximately 10.6 pounds/ft^3. Liquid oxygen cylinders also have the advantage of storing oxygen at lower pressures; however, cylinders for liquid storage must be well-insulated to decrease evaporation of the oxygen. Dewar vacuum containers are usually used for this purpose.

The primary objection to the liquid oxygen system is the problem of poor shelf life. In small containers (5000 ft^3 of gas STP) the daily boil-off is from 4 to 6 per cent of the remaining oxygen. In large containers (50,000-100,000 ft^3 of gas STP) the boil-off can be reduced to 1/2 to 1 per cent of the remaining volume. If a 5-per cent boil-off rate is assumed 40 per cent of the original oxygen will be lost after 10 days. If the boil-off rate is decreased to 1 per cent, 40 per cent of the gas will be lost in 51 days.

Figure 4 is a chart showing the per cent by volume of gas lost for various boil-off rates. The need for frequent replenishing of the oxygen is apparent even though a small boil-off rate can be obtained.

Liquid oxygen storage presents greater handling difficulties than high pressure cylinders. Contact of the liquid with human tissue causes serious damage, and contact with combustible materials such as oils creates an explosive hazard.

2.2.2 Chemical Methods of Oxygen Production

2.2.2.1 Chlorate Candles - Chlorate candles have been in existence for 30 years. Several German patents in the 1930's describe the development of a system which supplies oxygen from the decomposition of alkali metal chlorates or perchlorates. Later the British evaluated the method as a possible means of oxygen supply for submarines but discarded the idea because chlorine was produced in hazardous concentrations. In 1943 the U. S. Navy became interested in chlorate candles and work was initiated to develop a satisfactory candle. Candles can now be produced which have a safe level of chlorine production.

A typical formulation of a sodium chlorate candle is: (Ref. 19)

$NaClO_3$	80 per cent by weight
powdered iron	10
BaO_2	4
powdered Fiberglas	6
	100

Oxygen is produced according to the reaction;

$$NaClO_3 \longrightarrow NaCl + 3/2 \; O_2$$
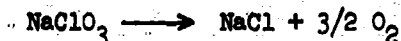
A small portion of the oxygen produced is used to oxidize the iron which in turn supplies the heat to sustain the reaction;

$$2Fe + O_2 \longrightarrow 2FeO$$
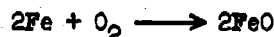
Since a small amount of chlorine is also produced from the decomposition of chlorates, barium peroxide is added to replace free chlorine with oxygen,

$$4NaClO_3 \longrightarrow 2Na_2O + 2Cl_2 + 5O_2$$

$$BaO_2 + Cl_2 \longrightarrow BaCl_2 + O_2$$
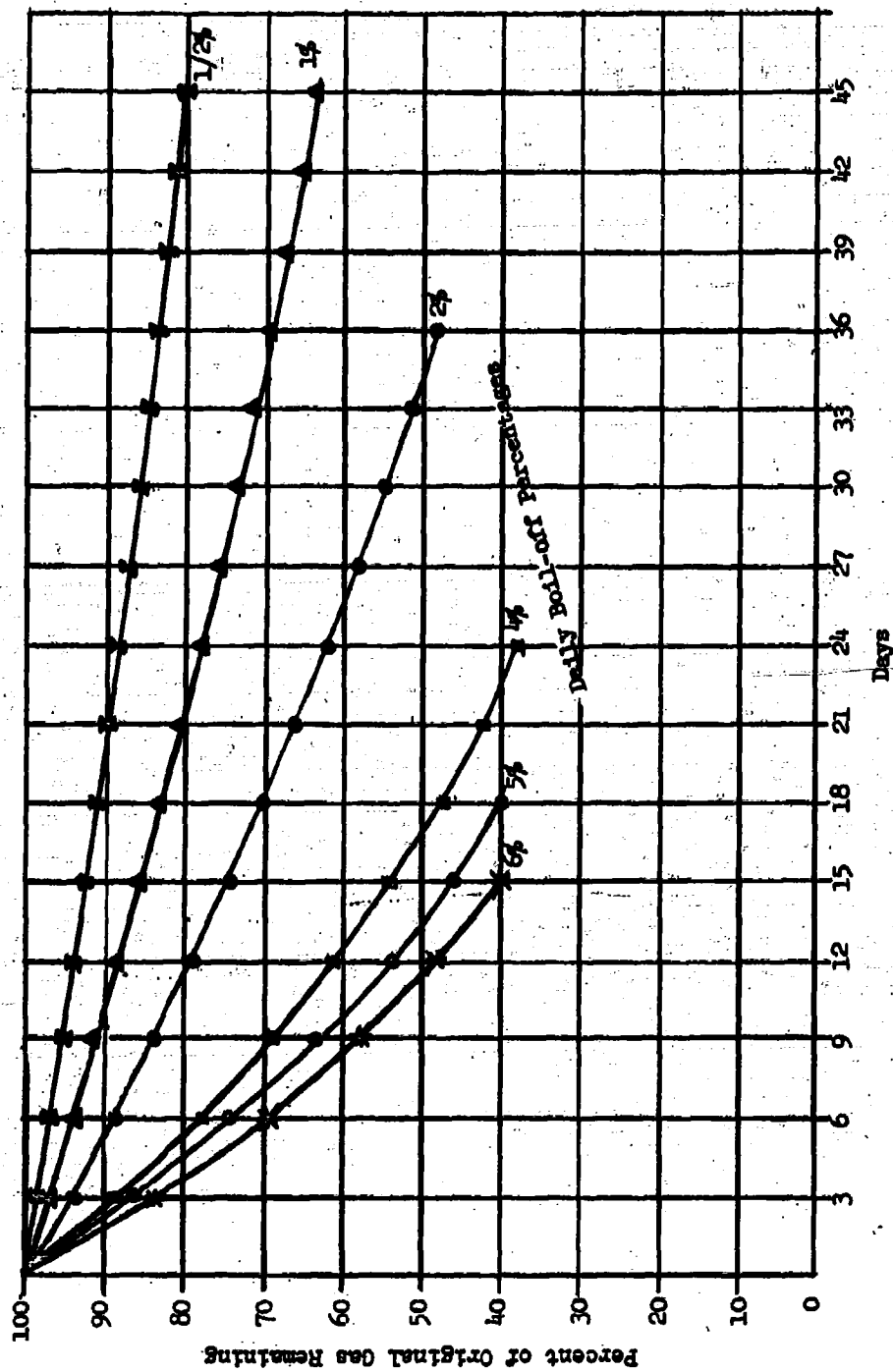
Figure 4. LIQUID OXYGEN DEPLETION RATES

The barium peroxide will hold the chlorine level to 5 ppm or below. The liberated gas is then passed through a bed of Hopcalite which further reduces the chlorine level to 1 ppm. (Ref. 20) This is considered to be a safe level. (Ref. 21)

The Fiberglas is added to serve as a binder because the reaction takes place at a temperature above the melting point of the chlorate. Before the Fiberglas is added in the formulation, it is baked to 750°F in order to remove volatiles which would form carbon monoxide.

The temperature of the reaction is from 1300 to 1500°F. Temperature can be controlled by varying either the percentage of the iron or barium peroxide in the formulation as shown in Figure 5. For a given composition and geometry, temperature will influence the rate of reaction. The rate of decomposition of $KClO_4$ is increased by factor of 1.6 for each 18°F increase in temperature. (Ref. 22)

Candles are generally made by molding or casting. In the original method the dry ingredients were mixed with 5 per cent water, molded at 5000 psi and dried at 212°F. In the casting method, the mixture is heated until the chlorate melts (491°F) and poured into molds of the desired shape. A cast candle has a higher density than a molded candle and thus will produce more oxygen for a given volume of candle.

Method Produced	Approximate Density (Ref. 23)
Cast	2.45 g/cc
Molded	2.0-2.2 g/cc

Approximately 1000 Btu are produced for every pound of oxygen liberated. (Ref. 24) This amounts to 83-100 Btu per man-hour.

The candles are available either as self-contained units which include the ignition system and the filters or as a candle which is burned in a special furnace. A diagram of each of these types are shown in Figures 6 and 7.

Candles which are burned in special furnaces are usually part of permanent installations where there is a continuous demand for oxygen. An example of this application would be aboard a submarine.

A small family-size chlorate candle is under development by Maywood Chemical Works which would supply sufficient oxygen for 48 man-hours. The cost of this unit should be approximately $10, plus $12 to $15 for the burner, so that the cost per man-hour would be about $0.50. The unit is self-contained and can be operated by following the directions on the unit.
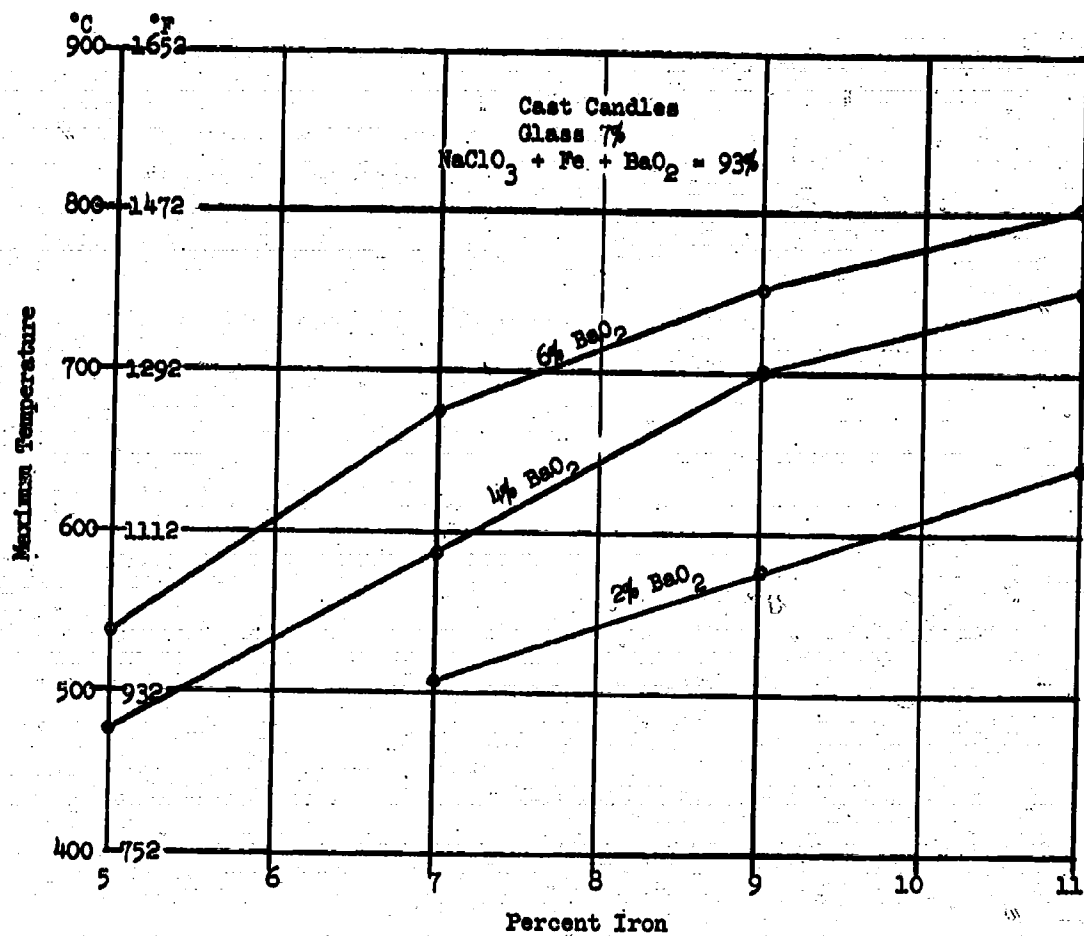
Figure 5   EFFECT OF BARIUM PEROXIDE AND IRON ON
MAXIMUM TEMPERATURE ATTAINED WITHIN CANDLE (Ref. 25)
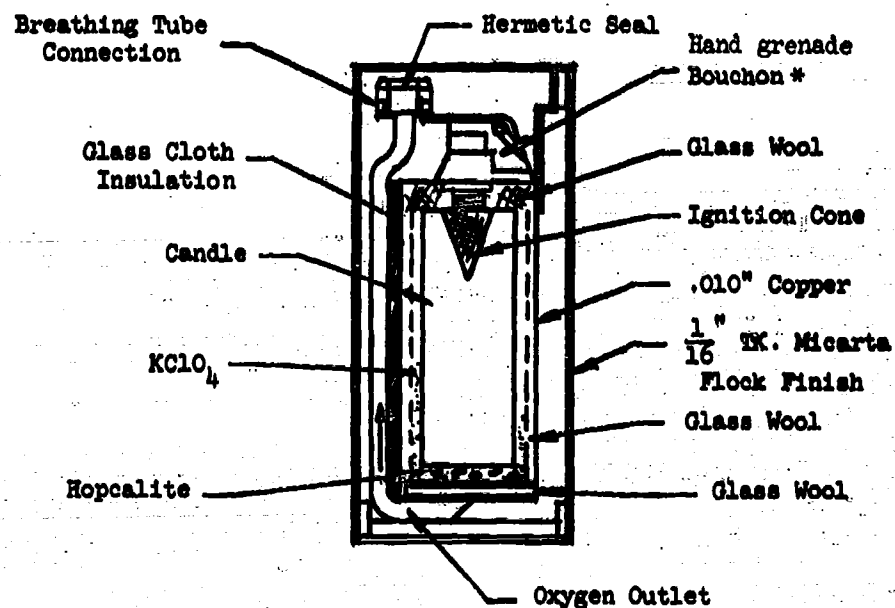
Figure 6   CONTAINED CHLORATE CANDLE

* Device similar to those used to trigger the fuse of a hand grenade.
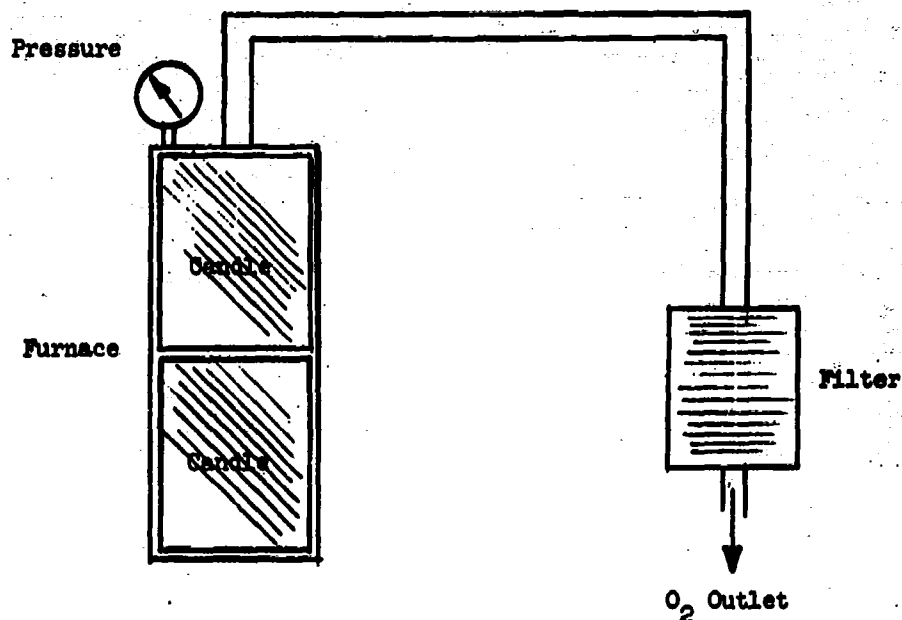
Figure 7   CHLORATE CANDLE FURNACE

A large self-contained unit is available from M.S.A. Research Corp. This candle liberates 90 ft^3 of oxygen over a period of 50 minutes; that is at a rate of 108 ft^3/hr. Since the rate of oxygen consumption is from 0.9-1.0 ft^3 per man-hour, this size candle would only be economically suitable for 100-person shelters or larger. The cost of the candle is $60.00 so per man-hour the cost would be $0.65 to $0.70. This candle is very easy to operate.

The submarine chlorate candle furnace may be considered for shelters with a capacity of 100 persons or more.

A furnace which burns round candles and liberates 120 cubic feet of oxygen per candle is now manufactured. A newer furnace design burns square candles. These candles liberate 150 cubic feet of oxygen. The production rate of oxygen is approximately 150 cubic feet per hour, thus one furnace would support approximately 150 persons.

COSTS

The cost of either the round or square furnace is $2000. The cost of a round candle, which has the capacity of 120 cubic feet of oxygen is,

Quantity	Price per Candle
1-11	$25.00
12-143	22.50
144-499	21.00
500 and over	20.00

The cost of the larger square candles was not available at the time of writing this report. This data is based on information from MSA Research Corporation.

All of the mentioned forms of chlorate candles have excellent shelf life. Candles have been stored for 15 years and performed satisfactorily. Also they can be operated over a wide atmospheric temperature range. In the range from -67°F to 77°F, the change in oxygen production is approximately 0.003 cubic ft/min°F. (Ref. 26) The chlorate candles deliver close to 34 per cent of their original weight as usable oxygen.

SAFETY

The self-contained chlorate candles are considered safe and easy to use by an untrained person.

The furnace and candle assembly, on the other hand, should be maintained by a trained or mechanically competent person since the furnace needs attention when the candles are changed. The furnace can reach temperatures up to 800°F with continued use, so there is danger of burns if someone were to come in contact with it.

2.2.2.2 Superoxides - Since the early 1930's, superoxides have been investigated for the purpose of supplying oxygen and absorbing carbon dioxide from a sealed environment. The primary field of interest was the atmospheric control aboard submarines; however, superoxide was considered unsatisfactory because of the material's explosive nature when it comes in contact with hydrocarbons, other organic chemicals or combustible substances. The material is currently being investigated as an oxygen source for both submarines and manned space vehicles.

Potassium superoxide is manufactured by the MSA Research Corporation. Molten potassium is sprayed into an atmosphere of dry air and the superoxide is formed as a canary yellow "fluff". This material is compacted, crushed and screened to the desired granule size. The 2-4 mesh material which is normally used in breathing apparatus has a bulk density of 41 lbs/ft^3. Theoretically, potassium superoxide will liberate 34 per cent of its original weight as oxygen. The guaranteed available oxygen is 32 per cent. (Ref. 27)

The basic equations for the reaction can be written,

1. $2KO_2 + H_2O \longrightarrow 2KOH + 3/2\ O_2$

2a. $2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$ or

2b. $2KOH + 2CO_2 \longrightarrow 2KHCO_3$
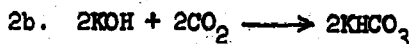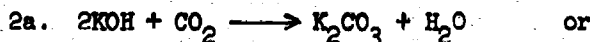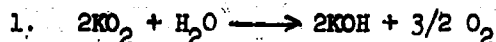
As explained in Section 2.1 of this report, the reactions should match a respiratory quotient of 0.82. A combination of equation 1 and 2a match and R.Q. of 0.67 and the combination of equation 1 and 2b match and R.Q. of 1.33. The following equation matches an R.Q. of 0.82.

3. $2KO_2 + 1.23CO_2 + 0.23H_2O \longrightarrow 0.77\ K_2CO_3 + 0.46\ KHCO_3$

$$+\ 3/2\ O_2$$
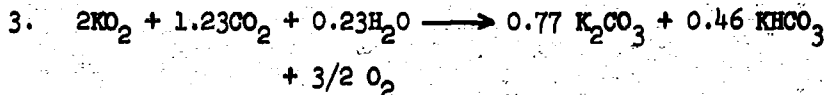
These equations indicate that water is necessary if the reaction is to take place. Experiments conducted by MSA Research Corp. support this theory (see Figure 8).

When dry carbon dioxide diluted with dry nitrogen was passed through a bed of potassium superoxide, some oxygen and water evolved and a hot zone was observed to advance from one end of the bed to the other. When the hot zone reached the end of the bed, all reactions stopped. (Ref. 28)
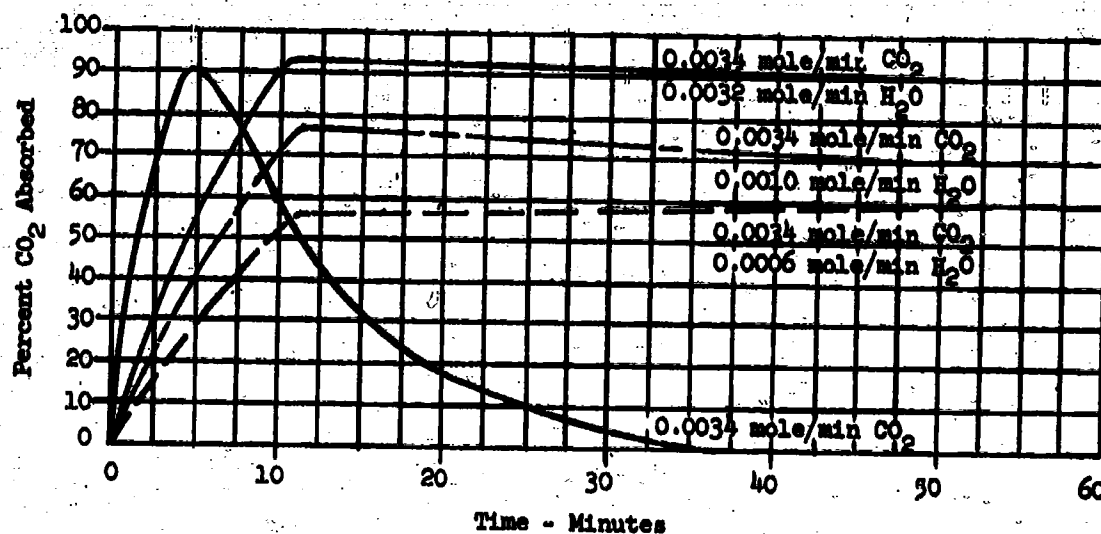
Figure 8 THE ABSORPTION OF CO_2 by KO_2 WITH VARIOUS
CONCENTRATIONS OF WATER VAPOR (Ref. 29)

The concentration of the water vapor present is one of several factors
influencing the ratio of carbon dioxide absorption to oxygen liberation in a
bed of potassium superoxide. The following table is an example of several
factors influencing the ratio.

Conditions Necessary to Yield CO_2/O_2 = 0.82 (Ref. 30)

KO_2 particle size	CO_2/H_2O, ratio by volume	Bed Temperature
2/4 mesh	2.5	77°F
4/6	1.4	140
10/20	2.0	77

Equation 3 on page 29 indicates that the ratio of CO_2 to H_2O should be
5.3 to 1 by volume; however, experimental data indicates that the working ratio
should be approximately 2.0 to 1. This indicates the water vapor is reacting in
other ways. Some other possibilities are, (Ref. 31)

$$K_2CO_3 + H_2O + CO_2 \longrightarrow 2KHCO_3$$

$$KOH + H_2O \longrightarrow KOH \cdot H_2O$$

$$K_2CO_3 + H_2O \longrightarrow K_2CO_3 \cdot H_2O$$

$$H_2O \longrightarrow \text{physically adsorbed}$$

$$H_2O \longrightarrow \text{passed through the bed without reacting}$$
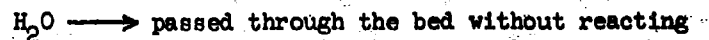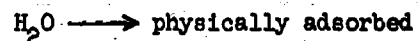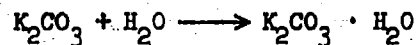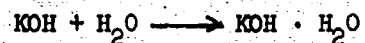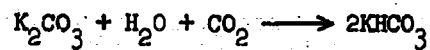
Therefore, if the concentration of carbon dioxide in the controlled environment is held at 2 per cent or 15 mm Hg, the water vapor should be 1 per cent or 7.5 mm Hg. At 75°F this value corresponds to a relative humidity of approximately 35 per cent (see Figure 9).
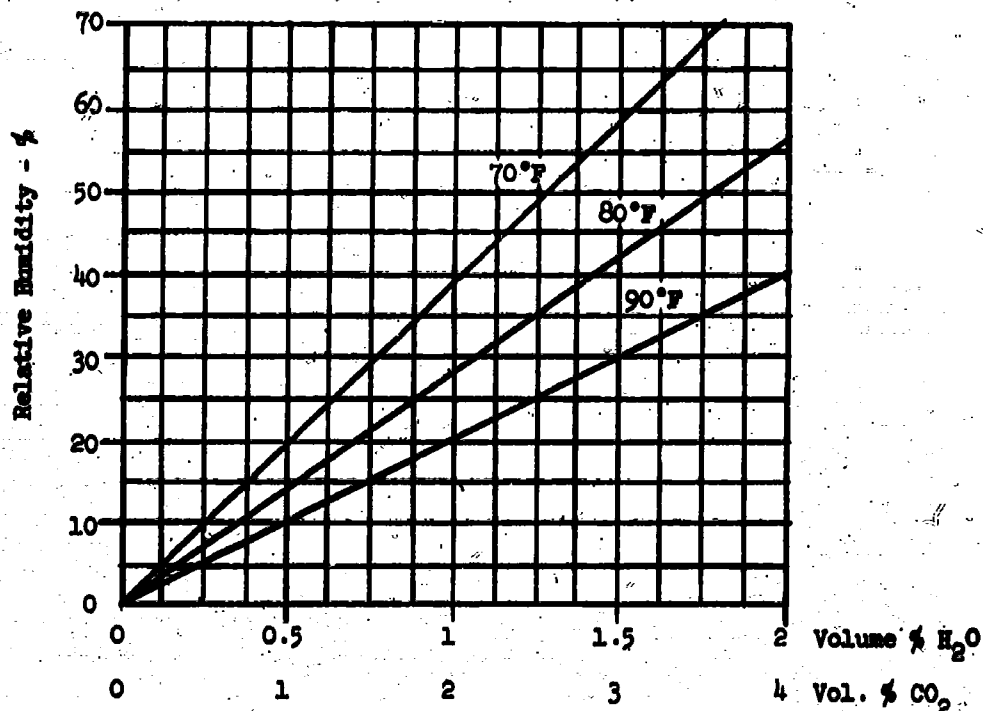
Figure 9 TEMPERATURE AND HUMIDITY EFFECTS UPON CO_2/O_2 RATIO IN BED OF KO_2

Since normal respiratory functions produce an excess of water, a desiccant is necessary to control the relative humidity and thus prevent an overproduction of oxygen.

A contradiction to this theory was observed when Project Hermes was conducted by the Air Force. Potassium superoxide was observed not to build up an oversupply of oxygen when tests were conducted with humans. (Ref. 32)

Heats of Reaction

Although the exact mechanism of the reaction is not known, approximation of the reactions and heats of reaction can be made.

$$12KO_2 + 6H_2O + 4CO \longrightarrow 4KOH + 4K_2CO_3 \cdot H_2O + 9\ O_2 \quad (Ref.\ 33)$$
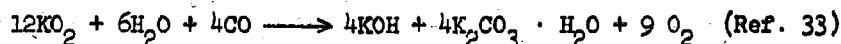
$$\Delta H = 250.7\ kCal.$$

$$heat\ liberated = 2560\ Btu\ per\ lb\ of\ CO_2$$

$$or \qquad 1570\ Btu\ per\ lb\ of\ O_2$$

$$or \qquad 256\ Btu\ per\ man\text{-}hour$$

The heats of various other reactions which can occur in a potassium superoxide bed are: (Ref. 34)

Reaction	Heat Evolved	Btu per lb of		
		O_2	H_2O	CO_2
$2KO_2 + H_2O \longrightarrow 2KOH + 3/2\ O_2$	9.4 KCal	350	940	---
$2KO_2 + CO_2 \longrightarrow K_2CO_3 + 3/2\ O_2$	43.1	1620	---	1770
$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$	33.7	----	---	1380
$KOH + CO_2 \longrightarrow KHCO_3$	33.1	----	---	1360
$4/3\ KOH + H_2O \longrightarrow 4/3(KOH \cdot 3/4H_2O)$	22.2	----	2200	----
$KOH + H_2O \longrightarrow KOH \cdot H_2O$	20.0	----	2000	----
$1/2KOH + H_2O \longrightarrow 1/2(KOH \cdot 2H_2O)$	16.9	----	1690	----
$2K_2CO_3 + H_2O \longrightarrow 2(K_2CO_3 \cdot 1/2H_2O)$	15.2	----	1520	----
$2/3K_2CO_3 + H_2O \longrightarrow 2/3(K_2CO_3 \cdot 3/2H_2O)$	15.2	----	1520	----
$K_2CO_3 + H_2O + CO_2 \longrightarrow 2KHCO_3$	33.8	----	3380	1380

Bed Temperature

Potassium superoxide can be used either in a static system or in a blower system. When the passive system is used, the bed temperature is usually never more than 40°F above the ambient atmospheric temperature; whereas in a blower-canister system the bed temperature can reach 600°F. (Ref. 35)

Hazards

As previously stated, superoxides are powerful oxidizing agents, thus any contamination of oils, organic compounds or combustible matter can form an explosive mixture if it comes in contact with the superoxide bed.

The lower bed temperature of a passive system reduces the fire hazard to some degree but at the same time it leaves a large surface area of exposed superoxide which could come in contact with combustible contaminants.

Superoxides cause severe burns if they come in contact with the skin. They are also very toxic if taken internally. In Project Hermes the dust of potassium superoxide was found to irritate the eyes so it was necessary to wear a protective mask when changing beds. (Ref. 36)

Other Superoxides

Sodium superoxide has been prepared and successfully tested for removing carbon dioxide and supplying oxygen. Theoretically, it can yield 43 per cent of its original weight as oxygen; whereas potassium superoxide can yield only 34 per cent.

The reactions of sodium superoxide generally produce a greater heat of reaction than the potassium compounds.

The reaction which approximates an overall reaction of a bed of superoxide (Ref. 37)

$$12NaO_2 + 6H_2O + 4CO_2 \longrightarrow 4NaOH + 4Na_2CO_3 \cdot H_2O + 9O_2$$
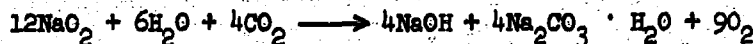
$$\Delta H = -307.2 \text{ kCal}$$

Heat liberated per lb of CO_2, 3140 Btu

Heat liberated per lb of O_2, 1915 Btu

Heat liberated per man-hour, 314 Btu

Other heats of reaction which can occur in a sodium superoxide bed are: (Ref. 38)

Reaction	Heat Evolved kCal	Btu per lb of		
		O_2	H_2O	CO_2
$2NaO_2 + H_2O \longrightarrow 2NaOH + 3/2\ O_2$	22.4	840	2240	---
$2NaO_2 + CO_2 \longrightarrow Na_2CO_3 + 3/2\ O_2$	52.1	1950	----	2130
$Na_2O_2 + H_2O \longrightarrow 2NaOH + 1/2\ O_2$	25.6	2880	2560	----
$Na_2O_2 + CO_2 \longrightarrow Na_2CO_3 + 1/2\ O_2$	55.3	6230	----	2260
$Na_2O + H_2O \longrightarrow 2NaOH$	46.8	----	4680	----
$Na_2O + CO_2 \longrightarrow Na_2CO_3$	76.5	----	----	3120
$NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$	29.7	----	----	1210
$NaOH + CO_2 \longrightarrow NaHCO_3$	30.1	----	----	1230
$NaOH + H_2O \longrightarrow NaOH \cdot H_2O$	15.4	----	1540	----
$Na_2CO_3 + H_2O \longrightarrow Na_2CO_3 \cdot H_2O$	13.7	----	1370	----
$1/7 Na_2CO_3 + H_2O \longrightarrow 1/7(Na_2CO_3 \cdot 7H_2O)$	13.3	----	1330	----
$1/10 Na_2CO_3 + H_2O \longrightarrow 1/10(Na_2CO_3 \cdot 10\ H_2O)$	12.8	----	1280	----

In order to match the metabolic R.Q. of 0.82, it is necessary to obtain the formation of the bicarbonate. Potassium bicarbonate is more stable than sodium bicarbonate for any given temperature.

Since sodium superoxide is available in only limited quantities and apparently has no advantage over potassium superoxide except on a weight percentage yield basis, no advantage can be seen at this time in preferring it over potassium superoxide in a fallout shelter.

Calcium superoxide and lithium superoxide have high theoretical percentages of available oxygen; however, they are not manufactured at the present time.

TABLE 6   OXYGEN CONTENT OF COMPOUNDS

Compound	Theoretical Available Oxygen
KO_2	34% by weight
NaO_2	43
CaO_4	46
LiO_2	61

Methods of Use

Tests performed in Project <u>Hermes</u> and at MSA Research Corporation indicate that 800 square inches of surface area are required per person for a passive system. This can be accomplished by having the material furnished in thin screens which are sealed with a plastic film. When the film is removed, the surface is exposed to the environment and the reactions commence.

For these experiments screens 20" x 10" x 1/2" with two exposed surfaces were used. Each container holds 9-10 pounds of superoxide and should last 27 man-hours since 1/3 pound of potassium superoxide is required per man-hour.

It must be kept in mind that at least two containers should be used for each person at all times so that sufficient surface area is exposed.

With a blower-canister system, the rate of carbon dioxide absorption can be controlled by the blower. The blower can be used continuously for a large group of people or intermittently for a small group. The only necessary equipment is the canister and the blower. More elaborate setups are available which include a flowmeter, and a timer to indicate when the canister is depleted. The blower can either be hand-driven or electrically driven.

MSA Research Corp. manufactures a canister which will accommodate from one to twenty persons. The canister will last for 72 man-hours. The cost per canister is $150.00 which amounts to $2.09 per man-hour. A blower costs from $50 to $300 depending upon type and accessories. MSA also sells the more elaborate setup described in the above paragraph for $2000.

Odor and Bacteria Removal

Besides removing carbon dioxide and supplying oxygen, potassium superoxide will also serve the purpose of removing odors and controlling the growth of bacteria. Tests conducted by MSA Research Corporation are described in Table 7.

2.2.2.3 <u>Hydrogen Peroxide</u> - Hydrogen peroxide is a powerful oxidizing agent that is used for many purposes. Dilute solutions are used as bleaches or disinfectants, while concentrations close to 100 per cent act as a monopropellant and can be used as a rocket fuel. These properties are based on the compound's property to readily decompose with the liberation of water, oxygen and heat.

Hydrogen peroxide decomposes according to the equation

$$H_2O_2(liq) \longrightarrow H_2O(liq) + 1/2\ O_2(gas).$$
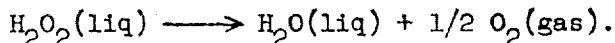
Heat of reaction $=$ 1240 Btu/lb of H_2O_2

or 2620 Btu/lb of oxygen.

TABLE 7 ACTIVITY OF KO_2 ON CONTAMINANTS

| Contaminant | | Mesh | Stream Concentration | | Residence Time | Results |
Compound	ppm		H_2O (%)	CO_2 (%)	(sec)	
Skatole	13	4-6	0.2	0.4	1.36	No detectable odor after 18 hrs.
Skatole	13	4-6	0.4	0.8	1.36	No detectable odor after 8 hrs.
Indole	13	4-6	0.4	0.8	1.36	No detectable odor after 7.5 hrs.
Indole	13	4-6	0.4	0.8	0.68	First detectable odor after 5 hrs.
Indole	13	14-20	0.4	0.8	0.68	First detectable odor after 7.5 hrs.
p-cresol	155	4-6	0.4	0.8	1.36	Not detectable after 8 hrs- trace odor after 11 hrs.
Methanol	1000	4-6	0.2	0.4	1.36	Removed 38% from stream
Methanol	1000	4-6	0.4	0.8	1.36	Removed 44% from stream
Acetylene	1000	4-6	0.2	0.4	1.36	No removal from stream
H_2S	1000	4-6	0.4	0.8	1.36	Immediate detectable odor
H_2S	100	4-6	0.4	0.8	1.36	First detectable odor after 60 minutes
H_2S	50	4-6	0.4	0.8	1.36	First detectable odor after 80 minutes

The heat of decomposition for solutions of various strengths is shown in Figure 10. Physical properties are shown in Table 8.
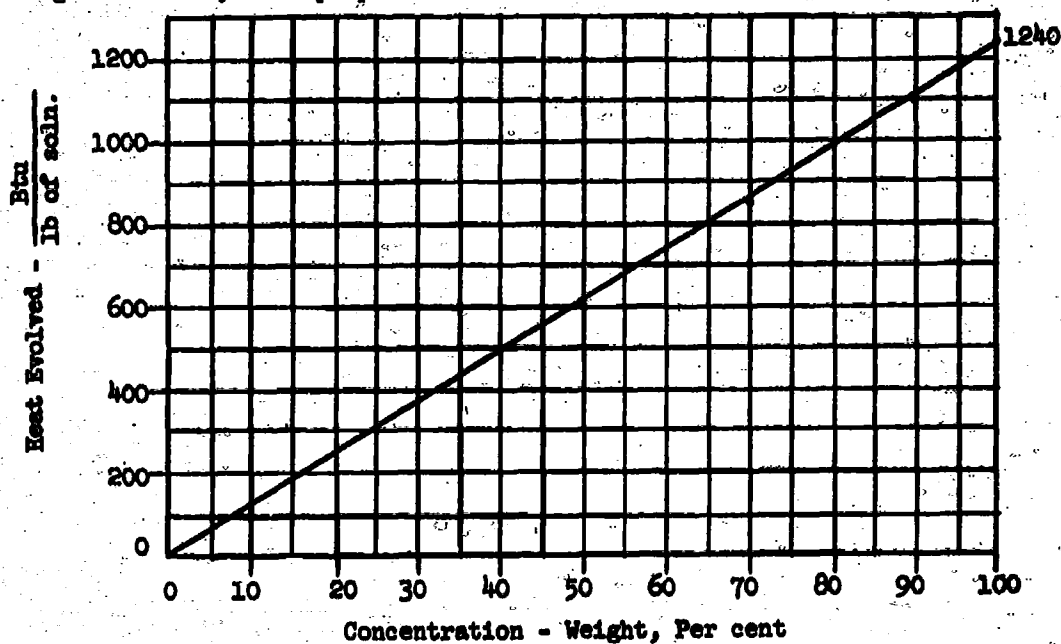
Figure 10 ...HEAT OF DECOMPOSITION FOR VARIOUS
SOLUTIONS OF H_2O_2

TABLE 8

PHYSICAL PROPERTIES OF HYDROGEN PEROXIDE (Ref. 39)

Concentration, wt per cent	50	70	90	98	100
Density at 77°F, g/cc	1.19	1.28	1.39	1.43	1.44
B.P. at 1 atm, °F	237.0	257.8	286.2	299	312.4
Heat of decomposition Btu/lb of solution, H at 77°F	603	852	1108	1214	1240
Heat of vaporization at 77°F Btu/lb of solution	869	788	700	662	653

29

Temperature of Reaction

The decomposition of concentrated hydrogen peroxide can reach very high temperatures if it is not controlled. An approximation of this temperature can be derived from the following equation.

$$T = \frac{H + Q_1 h_1}{Q_2 Cp_2}$$

where,

T = temperature, °F

H = heat of reaction, Btu

Q_1 = quantity of reactants, lbs

h_1 = sensible heat of reactants, Btu/lb

Q_2 = quantity of products, lbs

Cp_2 = mean specific heat of products, Btu/lb °F

This equation assumes that there is no heat transfer to the reactor or surroundings. Some typical values are listed below.

Concentration of H_2O_2	Theoretical Decomposition Temperature
75% (wt)	800-850°F
90%	1300-1400
98%	1700-1800

Although H_2O_2 has a high theoretical decomposition temperature, it can be decomposed in a controlled converter at 300°F. (Ref. 40)

Most heavy metals or contaminants will catalyze the reaction. Some substances which are very active in catalyzing the reaction are the permanganates of sodium, potassium or calcium, manganese dioxide, platinum, and iron oxide. Most impurities, dusts, or enzymes present in the containers or apparatus will also catalyze the reaction.

Because water is a product of the reaction, hydrogen peroxide is able to produce 0.53 lbs of steam for every pound of peroxide decomposed or 1.13 lb of steam for every pound of oxygen produced. The steam can be used to generate power via a turbine and can be condensed to provide drinking water. By the same token, the water must be condensed, or else the air in the environment will become saturated with excess moisture.

To yield one man-hour of oxygen, the following requirements are necessary.

Concentration, wt%	50	90	98	100
Lbs peroxide to yield 1 lb of O_2	4.24	2.36	2.17	2.12
Lbs peroxide/man-hr at .083 lb O_2/man-hr	0.352	0.198	0.180	0.176
Volume, gallons per man-hour at 80°F	0.0355	0.0173	0.0150	0.0146
Material cost $/lb; tank car/drum	.26/.30	.50/.615	.60/1.0	
Material cost $/man-hr; tank car quantities	.092	.099	.108	
Material cost $/man-hr; drum quantities	.106	.122	.18	

In addition to the cost of the material, special high purity aluminum containers must be purchased. If the H_2O_2 is obtained in 30-gallon drums, a charge of $100 is made per drum plus a charge of $50 for the delivery syphon. Since one drum of 98 per cent hydrogen peroxide would supply 2000 man-hours, an additional charge of $0.05/man-hour would be required for this concentration. The 90-per cent peroxide drum would provide 1734 man-hours so the additional charge would be $0.058/man-hour.

Hazardous Aspects of Hydrogen Peroxide*

Toxicity - Neither hydrogen peroxide solutions nor their vapors are considered toxic. Both will act as an irritant, however, the vapors being very discomforting to the eyes, nose and throat. Contact with the liquid results in a stinging sensation accompanied by a whitening of the affected area. This irritation quickly subsides and the skin gradually regains its color, providing contact time is short. Extended contact is likely to result in a serious and slow healing burn. Thorough and immediate washing with large amounts of water will greatly lessen the possibility of serious injury by diluting the peroxide and reducing the length of contact time. In the event that the eyes are contacted, immediate irrigation with copious quantities of water is necessary. Thus, it is advisable to have eye-wash fountains and safety showers in all areas where peroxide is handled. A physician's assistance should be sought as soon as possible in cases of serious burns and in all instances where eye contact is made.

Fire - Isolated peroxide solutions, regardless of concentration, are non-flammable. However, solutions above 65 weight per cent H_2O_2 are very strong oxidants and may induce the spontaneous ignition of many combustible materials.

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* This section abstracted from Solvay Technical and Engineering Bulletin No 19, pp 51-54.

Concentrations of less than 60 per cent do not exhibit this tendency on initial contact with combustibles. On prolonged contact, however, water evaporates more rapidly than the hydrogen peroxide, resulting in a residual solution with a peroxide concentration which may exceed the 65 per cent "safe" limit. Because of these considerations, it is unsafe to store combustible organics and materials such as wood, paper, or rags near H_2O_2 lines or handling areas. Where possible, storage areas should be of fireproof construction, particularly for concentrations above 52 weight per cent. An adequate supply of water should also be available in all handling and storage areas for emergencies. Water may be used to flush away any spillage and to gight most fires involving H_2O_2. Of course, water should not be used on electrical or oil-type fires regardless of the presence of peroxide.

Explosion - Experimentation indicates that it is not possible to detonate even the most concentrated hydrogen peroxide solutions by such methods as mechanical drop-weight tests, rifle and machine gun bullet impact trials, and blasting cap studies with and without booster charges. However, at atmospheric pressure, vapors containing above 26 mole per cent hydrogen peroxide (40 wt. per cent) can be explosive.

When mixed together, combinations of the higher strengths of hydrogen peroxide and a number of organic materials will detonate with an explosive force approaching that of nitroglycerin. Of additional concern is the tendency of a number of mixtures to give no indication of reaction when added together, but to detonate if subjected to mechanical shock or slight increases in temperature. These latent tendencies make extreme care an absolute necessity when experimenting with hydrogen peroxide.

The accelerating effect of contamination on the decomposition rate of peroxide has been described earlier. As mentioned, the heat released in the reaction raises the solution temperature, which in turn leads to further decomposition. This cycle rapidly gains impetus and if uncontrolled may result in a pressure build-up of sufficient magnitude to rupture a containing vessel. For this reason, it is recommended that storage tanks and other collection vessels be equipped with temperature recording apparatus which will signal undesirable temperature increases. When an appreciable temperature rise is detected, it may be possible to control the reaction by cooling the tank or vessel externally with water. If the peroxide is not too badly contaminated, it may also be possible to prevent excessive decomposition by adding packaged stabilizers (for example, sodium stannate) directly to the product in storage. Where these measures fail, it becomes necessary to pump large quantities of water directly into the tank and to dump tank contents into a drain with additional dilution.

Recommended Handling Procedures - Before any work involving hydrogen peroxide is initiated, it is necessary for all interested personnel to thoroughly familiarize themselves with the properties of the product. It is advisable to conduct original experimentation behind protective screens or barriers using small controlled quantities of reactants until definite behavior patterns have been established for the reaction. Education of all laboratory technicians, workmen and operators in the proper method of handling H_2O_2 will serve to greatly minimize the possibility of accidents.

During laboratory experimentation with this oxidant, the following proce-
dures should be observed:

1. Peroxide samples should be stored in pyrex bottles. Polyethylene
    containers may also be used although they are not recommended for
    the handling of high strength material (> 52 per cent) because of
    the potential danger associated with the solubility of this resin
    in peroxide. Equipment must be of acceptable materials and should
    be properly cleaned and passivated prior to use.

2. All peroxide samples should be stored in areas which are inacces-
    sible to unauthorized personnel. Bottles should be shelved so as
    to minimize the dangers of spillage and breakage. Sample bottles
    should have appropriate labeling and should be vented or covered
    with aluminum foil or clean glass beakers. They should NEVER be
    stoppered.

3. Unused aliquots should never be returned to the original sample
    but should instead be flushed down a drain with large amounts of
    water.

4. In the laboratory, goggles and Neoprene or Koroseal gloves must
    be worn whenever peroxide is being handled. Because the ordinary
    clothing may contain enough catalytic contamination to constitute
    a fire hazard, protective aprons of polyvinyl chloride or poly-
    ethylene are advisable.

5. Any spillage in the laboratory should be flushed immediately with
    water.

The over-all safety precautions outlined for laboratory handling are
generally applicable to plant scale operations. The protective clothing for
plant personnel should also include rubber boots and a complete outer garment
of Dacron. Orlon has also been tested as a fabric for garment purposes and,
although not as suitable as Dacron, is acceptable. Additional equipment such
as a face mask or helmet can be worn, although this in itself may prove dangerous
by virtue of the restrictions thus placed on the worker's movements.

In view of the foregoing it seems unlikely that hydrogen peroxide would be
incorporated for supply of power, water, or oxygen at the present state-of-the
art. However, further research and development activity may indicate methods
to obviate the chemical's hazardous properties and utilize its advantages.

2.2.2.4 <u>Other Peroxides</u> - Sodium peroxide reacts with water to yield
sodium hydroxide and hydrogen peroxide. The hydrogen peroxide decomposes to
yield water and oxygen as described in Section 2.2.2.3.

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

$$H_2O_2 \longrightarrow H_2O + 1/2\ O_2$$

Overall reaction $Na_2O + H_2O \longrightarrow 2NaOH + 1/2\ O_2 + 29{,}700$ Btu at $77°F$
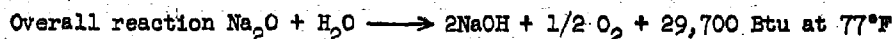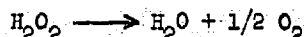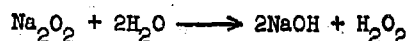
This reaction liberates 1860 Btu per pound of oxygen produced or 154 Btu per man-hour.

Since NaOH is also produced, carbon dioxide can be absorbed in the process. An overall reaction written for an R.Q. of 0.82 is

$$Na_2O_2 + 0.58\ H_2O + 0.41\ CO_2 \longrightarrow 1.18\ NaOH + 0.41\ Na_2CO_3 + 0.5\ O_2$$
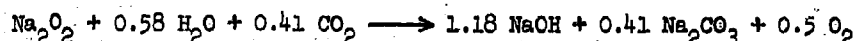
$$\Delta H = -57{,}500 \text{ Btu at } 77°F$$

This is equivalent to 3590 Btu per pound of oxygen liberated, 3190 Btu per pound of CO_2 absorbed or 300 Btu per man-hour.

Sodium peroxide can also be decomposed at $860°F$ without the addition of water according to the reaction

$$Na_2O_2 \longrightarrow Na_2O + 1/2\ O_2$$

Heat is required to make this reaction proceed to the right. This amounts to 34,500 Btu or 2160 Btu absorbed per pound of oxygen liberated.

Sodium peroxide is similar to sodium superoxide in that it reacts with water to liberate oxygen and then absorbs carbon dioxide. Mixtures of sodium peroxide and potassium superoxide have been prepared in order to match the metabolic R.Q. of 0.82.

Like the superoxides, peroxides are toxic compounds. Likewise they are fire hazards since the presence of water will liberate hydrogen peroxide. On a weight basis, 4.88 lbs of sodium peroxide are required to liberate 1 lb of oxygen while 2.95 lbs of KO_2 will liberate the same quantity of oxygen.

An advantage of sodium peroxide is its relatively low cost. Drum lots (lcl) cost approximately $0.22 per pound which amounts to $0.108 per man-hour. This is in the same price range as hydrogen peroxide and much cheaper than potassium superoxide. The advantage over hydrogen peroxide is in storability, handling, and safety of spilled material. The main drawback is in matching the metabolic R.Q.; for this superoxide is superior.

Calcium peroxide will also react with water to yield H_2O_2 which decomposes to water and oxygen. Theoretically 4.5 lbs of CaO_2 are required to produce 1 lb of oxygen. This slight advantage over sodium peroxide is nullified by the higher cost of the calcium peroxide. Drum quantities cost from $0.78 to $1.60/pound which would amount to $0.35 to $0.72 per man-hour.

2.2.2.5 <u>Electrolytic Methods</u> - Hydrogen and oxygen can be obtained from water by passing a direct current through it. There exist various types of cells for carrying out this reaction; however, they have the same overall reaction.

$$H_2O \longrightarrow H_2 + 1/2\ O_2$$
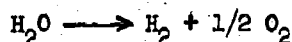
The hydrogen which is produced is nontoxic but must be eliminated because it is a fire hazard.

Theoretically, 1520 amp-hrs of power are required to produce one pound of oxygen. Therefore, the power requirements per person are 126 amps per hour. The commercial H_2-O_2 production cells operate at 1.5 to 2.5 volts. The electrolyte is a solution of 15 per cent NaOH or the equivalent concentration of KOH. For one ft^3/hr of oxygen, 200-300 watts are needed.

2.2.2.5.1 <u>Treadwell Cell</u> - For submarine application the Treadwell cell, which is a modification of the commercial cell, has been developed. This is a high pressure unit which operates at 3000 psi, 200°F, 750 amperes and 3.0 volts. A single cell will support 9-10 men by electrolyzing 3 gallons of water per day. The hydrogen is collected under pressure and pumped overboard.

2.2.2.5.2 <u>Split Cell</u> - Another type of cell is the nickel-cadmium split cell. This cell has the characteristic that only one gas is released at a time. During the discharge cycle the following reactions take place at the electrodes:

$$Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^-$$
$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$$
$$\overline{Cd + 2H_2O \longrightarrow Cd(OH)_2 + H_2}$$
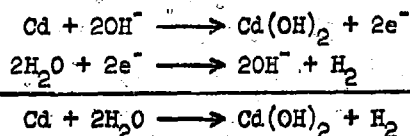
No oxygen is produced during discharge so the hydrogen can be collected and discarded. During the charging phase the reactions are:

$$Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-$$
$$2OH^- \longrightarrow H_2O + 1/2\ O_2 + 2e^-$$
$$\overline{Cd(OH)_2 \longrightarrow Cd + H_2O + 1/2\ O_2}$$
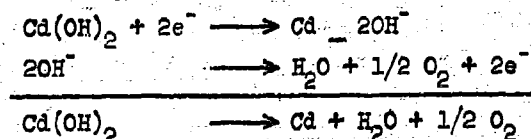
No hydrogen is produced during discharge so the oxygen can be used as it is evolved.

A unit designed for 100 men aboard a submarine consists of two banks of 125 cells each. Each bank operates alternately at 100 amperes and 275 volts. The entire unit weighs 4100 pounds and occupies 34.5 cubic feet. (Ref. 41)

2.2.2.5.3 Sodium Sulfate Electrolytic Process - The sulfate process is a three-step operation in which hydrogen and oxygen are produced and carbon dioxide is absorbed by the sodium hydroxide formed in the electrolyzer. A flow diagram for the process is shown as follows. (Ref. 42)
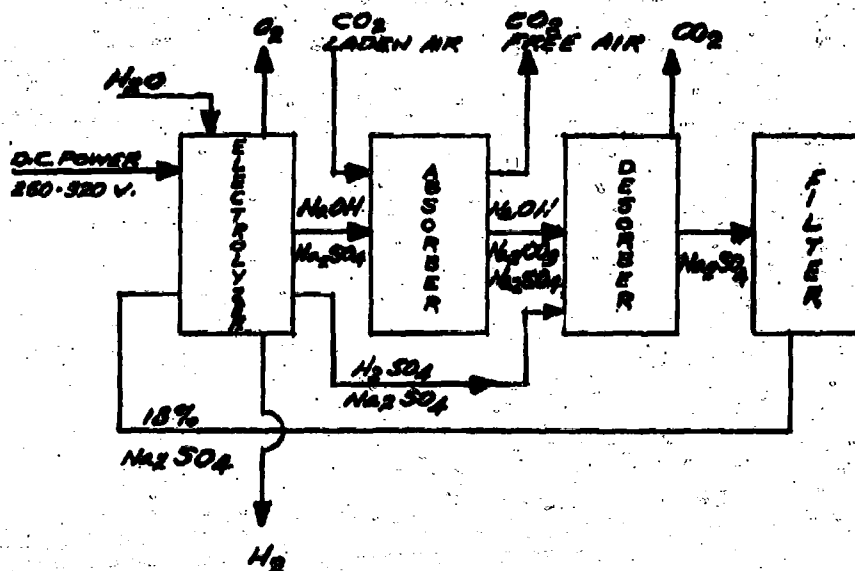
Figure 11 THE SULFATE ELECTROLYTIC PROCESS

The following electrochemical reactions take place in the electrolyzer.

Anode: $2SO_4^{--} + 2H_2O \longrightarrow 2H_2SO_4 + O_2 + 4e^-$

Cathode: $4Na^+ + 4H_2O + 4e^- \longrightarrow 4NaOH + 2H_2$
_____

$4Na^+ + 2SO_4^{--} + 6H_2O \longrightarrow 2H_2SO_4 + 4NaOH = 2H_2 + O_2$
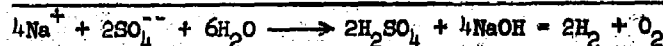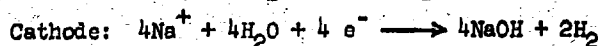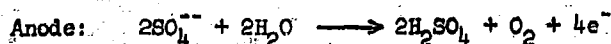
In the absorber the chemical reaction is

$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$
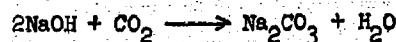
In the desorber the chemical reactions are

$Na_2CO_3 + H_2SO_4 \longrightarrow CO_2 + Na_2SO_4 + H_2O$

$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$
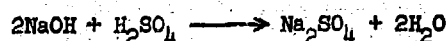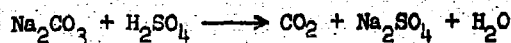
The overall reaction for the absorber and the desorber is:

$$4NaOH + 2H_2SO_4 \longrightarrow 2Na_2SO_4 + H_2O$$
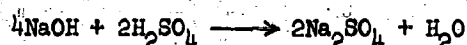
The overall reaction for the entire process is

$$2H_2O \longrightarrow 2H_2 + O_2$$
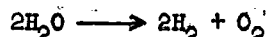
According to the reactions shown, twice as much NaOH is produced as is needed to remove the carbon dioxide from the air. This will allow for incomplete absorption and still leave sufficient capacity to remove all of the carbon dioxide.

Experimental runs have shown that to liberate one cubic foot of oxygen, 700 watt-hours of electrical power are needed. This is equal to 650 watts per man-hour which is three times the power requirement of other electrolytic processes; however, carbon dioxide is not removed in the other systems.

Although the sulfate cycle can be run satisfactorily, it should be considered as being in the development stage because more data is needed to obtain the optimum design and operating conditions.

The chemicals needed for the sulfate cycle are water and sodium sulfate. The amount of sulfate depends upon the size of the equipment, but the cost of this will be very small when compared to the cost of the equipment together with the electrical machinery that is required.

2.2.2.6 Photosynthesis - In the presence of light, green plants such as algae absorb carbon dioxide and release oxygen.

Much work has been done in testing various species of algae and different environments to produce the maximum growth rate.

Hannan and co-workers studied the Sorkin Strain of Chlorella pyenoidessa. The optimum temperature for growth of this strain was found to be 98-102 °F. (Ref. 43) Also lighting and method of lighting are important. The reaction of Chlorella in the absence of light is the opposite of the reaction in the presence of light.

$$\frac{\text{Rate of } CO_2 \text{ to } O_2 \text{ conversion in light}}{\text{Rate of } O_2 \text{ to } CO_2 \text{ conversion in darkness}} = 20 \qquad \text{(Ref. 44)}$$

Other factors influencing the rate of conversion are type of lighting, spacing of lights, type of nutrients, degree of agitation, and concentration of suspension.

Hannan found that the maximum rate of conversion is 250 ml of oxygen per hour for each liter of suspension. Therefore each person would require 33.5 gallons of suspension under optimum conditions.

The disadvantages of the photosynthesis process are:

1. Close control of environment is needed to achieve optimum conversion.

2. A loss of light would stop the process, and a small change in temperature can kill the algae.

3. The process is unreliable. Experimenters have had cultures die for no apparent reason. (Ref. 45)

4. A large volume of suspension is required to support each person.

2.2.2.7 **Regenerative Oxygen Containing Chemicals** - Certain complex compounds have the property of combining with molecular oxygen and releasing it upon heating. More prominent among these is the chelate salicylaldehyde ethylendiamine cobalt, known as "Salcomine".

The compound is oxygenated at low temperatures and under pressure and deoxygenated at elevated temperatures and under reduced pressure.
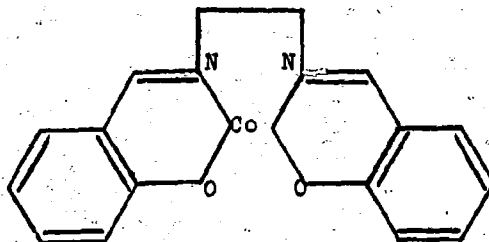
Several compounds derived from salicylaldehyde and similar to Salcomine were found to be more active. However, with the exception of a fluorine-substituted compound, they are inferior in stability and oxygen capacity.

Because shelters require a single supply of oxygen, the use of a regenerable oxygen-storing chemical is not of interest unless it is economically superior to other nonregenerative systems.

Theoretically one atom of oxygen can be released from one molecule of chelate. Therefore, Salcomine should release five per cent of its weight as oxygen. Materials manufactured on a pilot plant scale have realized a capacity of 95 per cent of the theoretical.

On this basis, at least 50 pounds of Salcomine would have to be stored per person. Although no data is available on the price of Salcomine, the starting material, salicylaldehyde, costs $1.23 per pound in carload quantities, so it is apparent that Salcomine would be more expensive than this. This is uneconomical when compared to other oxygen supply methods.

In addition to being a more expensive oxygen supply method, Salcomine produces a dust which is toxic and irritating to the bronchial and digestive system. (Ref. 46) This method will not be further considered as a source of oxygen.

2.2.3 Comparison of Oxygen Supply Systems

Oxygen supply systems will be compared from the standpoint of reliability, power requirements, costs, and handling and storage convenience. The reader is referred to Table 9 for the summarization of this comparison.

TABLE 9

COMPARISON OF OXYGEN SUPPLY METHODS

Method	Cost-$/man-hr	Heat Liberated- Btu/man-hr	Reliability and Safety
High Pressure Gas Storage	0.20-0.35	Slight negative	Excellent
Liquid Storage		-8	Poor
Chlorate Cndls.	0.50-0.67	85	Good
Potassium Superoxide	0.67 plus equipment	256	Fair
Hydrogen Peroxide (90%)	0.16-0.18	117	Poor
Electrolysis	High Equipment Cost	-	Poor
Photosynthesis	High Equipment Cost	Slight positive	Poor

Reliability is considered of prime importance in ranking the oxygen supply systems. Gas storage cylinders have been used extensively in aircraft and hospitals and have yielded reliable service. Chlorate candles have been used successfully in submarines in emergencies with good results. Extensive laboratory tests by various investigators have shown potassium superoxides to be a reliable source of oxygen. Peroxides have not been as extensively investigated and are considered difficult to control.

Systems considered to have poor reliability include liquid oxygen converters, electrolysis cells, and photosynthetic devices. Liquid oxygen is subject to an unavoidable evaporation rate which makes the reliability dependent upon constant replenishment during storage.

Electrolysis is only as reliable as the source of electrical power. Because a large electrical supply will not necessarily be available, this method is not considered reliable. Photosynthesis has demonstrated poor reliability in the laboratory.

Power Requirement

High pressure gas cylinders and chlorate candles require no power. Liquid oxygen requires very low amounts of power for evaporation. Superoxide canisters require air circulation when in operation, but this can be accomplished with a hand blower so no auxiliary power is necessary.

The decomposition of hydrogen peroxide can be promoted in the presence of a catalyst alone. Similarly, solid peroxides require no power.

Electrolysis systems require 200 to 300 watts of power per person and thus considered to have high power requirements. Photosynthesis requires a controlled temperature and a source of high intensity light.

Storage and Handling

High pressure gas cylinders can be stored for long periods of time and are easily operated by simply opening a valve. The cylinders should be periodically checked to make sure that the gas has not escaped.

Liquid oxygen should be eliminated from further consideration because of the problem of boil-off.

Chlorate candles in self-contained units have an indefinite shelf life and are easily started by pulling a pin, whereas the chlorate candles burned in furnaces should be handled by trained personnel.

Superoxide in canisters is storable as long as the canisters remain sealed. The use of a canister and blower is easily accomplished safely as long as contaminants of hydrocarbons or other combustible matter do not come in contact with the bed. Loose superoxide in screens without a blower is not recommended because of the danger that combustible contaminants would form an explosive mixture.

Peroxides are hazardous to handle for untrained personnel and should not be considered further.

Electrolysis equipment can be stored in a dormant state for long periods of time, however, a lack of electrical power would make the equipment useless. Since electrolysis produces hydrogen, an explosive hazard would be present.

Photosynthesis requires a constant control of temperature and source of light even when being stored and thus would require constant control which is uneconomical.

In view of the foregoing only stored gas systems, and chlorate candles will be considered during the remainder of this report.

2.3 Carbon Dioxide Removal

Carbon dioxide can be removed from an environment by a number of methods. These include:

1. Chemical absorption in a bed of solid granules.

2. Absorption in a liquid with chemical reaction.

3. Physical adsorption.

4. Diffusion of gases through a membrane.

5. Freeze-out techniques.

2.3.1 Solid Absorbents

Solid absorbents include alkali oxides or hydroxides, alkaline earth oxides or hydroxides. In the presence of moisture these materials are bases while in the presence of moisture carbon dioxide forms a weak acid. Thus the reaction is neutralization.

2.3.1.1 Superoxides - Alkali superoxides are described in Section 2.2.2.2 where they were considered as a source of oxygen.

2.3.1.2 Lithium Hydroxide - Lithium hydroxide is a white crystalline base which can be used to remove carbon dioxide. The U.S. Navy has used the anhydrous form as an emergency carbon dioxide absorber aboard submarines since the 1930's. Lithium hydroxide is presently being used aboard the Project Mercury space capsules.

The equation for the reaction is

$$2LiOH + CO_2 \longrightarrow H_2O + Li_2CO_3 .$$
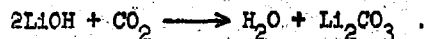
If the water is assumed to evolve in the liquid state, the heat of reaction is 1310 Btu per pound of carbon dioxide or 131 Btu per man-hour.

It is more probable that the reaction will evolve the water in the gaseous state. In this case the heat of reaction would be 875 Btu per pound of carbon dioxide or 87.5 Btu per man-hour. This reaction takes place efficiently at temperatures as low as 35°F. This is lower than the effective temperature limit of most other absorbents. Theoretically, one pound of lithium hydroxide will absorb 0.92 pounds of carbon dioxide.

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Assuming a carbon dioxide production rate of 0.1 lb per man-hour and a reaction efficiency of 90 per cent, 0.12 pounds of lithium hydroxide would be required per man-hour. On the basis of a 24-hour period of being sealed from the outside atmosphere, 2.9 pounds of lithium hydroxide must be stored for each person.

Lithium hydroxide can be used either passively or in a blower-canister system. In the passive system, the granules are spread in a thin layer over a screen or flat container so that a large surface area is exposed. The blower-canister system could be similar to that used for superoxides. The air is blown through the bed, reacted, filtered and released back into the atmosphere. The blower can be hand-driven or electrically powered. For a small number of persons, intermittent operation is sufficient whereas for a large group, continuous operation is necessary.

Hazards

Lithium hydroxide is a strong caustic material which will cause burns if it contacts the skin, especially if the skin is moist. The eyes are very susceptible to irritation caused by lithium hydroxide dust. As with all strong bases, lithium hydroxide will react violently if it comes in contact with strong acids.

The material can be pelletized or granulated. A 4-8 or 8-10 mesh granule will have less tendency to dust than a very fine material. Because lithium carbonate has a very high temperature of decomposition, lithium hydroxide is classified as a nonregenerative chemical. Lithium hydroxide is expensive; however, it can be used without any auxiliary equipment so it can still be considered. The anhydrous material costs from 4 to 5 dollars per pound. This amounts to 50 to 60 cents per man-hour.

2.3.1.3 _Baralyme_ - Baralyme is a crystalline caustic mixture which will absorb carbon dioxide.

The composition of the material is (Ref. 47)

20 per cent (wt)	$Ba(OH)_2 \cdot 8H_2O$
80	$Ca(OH)_2$
small amount	KOH
trace	Mimoza Z dye + ethyl violet
trace	wetting agent

The $Ba(OH)_2 \cdot 8H_2O$ provides water of crystallization which acts as a binder and also sustains the reaction with carbon dioxide. When the $Ba(OH)_2 \cdot 8H_2O$ reacts with carbon dioxide, $BaCO_3$ forms with a sufficient amount of water to wet the KOH and $Ca(OH)_2$ and sustain the reaction.

The bulk of the material is calcium hydroxide. This reacts with carbon dioxide in the presence of an activator, such as sodium or potassium hydroxide, to form calcium carbonate. The dye is added to the formulation to indicate when the absorbing power of the material is depleted. Fresh material is pink. The color then shifts first to purple and then to blue as salts of weak acids are formed. (Ref. 48) The small quantity of wetting agent is added to reduce the tendency to dust.

Heat of Reaction

For the reaction,

$$Ba(OH)_2 \cdot 8H_2O + CO_2 \longrightarrow BaCO_3 + 9H_2O_{liq},$$
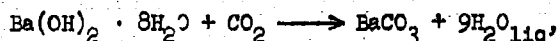
the heat of reaction at 77°F is 508 Btu per pound of CO_2 or 70.8 Btu per pound of $Ba(OH)_2 \cdot 8H_2O$. This is based on the assumption that all the water is evolved as a liquid.

For the reaction,

$$Ca(OH)_2 + CO_2 \xrightarrow{H_2O} CaCO_3 + H_2O,$$
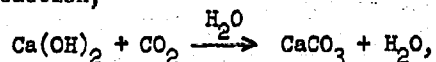
the heat of reaction at 77°F is 1055 Btu per pound of CO_2 or 627 Btu per pound of calcium hydroxide. This is also based on the assumption that the water is evolved as a liquid.

Constituent	Btu (lb)	Weight (%)	Heat Liberated	Absorbed CO_2/lb	Total CO_2 Absorbed
$Ba(OH)_2 \cdot 8H_2O$	70.8	20	14.2	0.140	0.028
$Ca(OH)_2$	627	80	502	0.594	0.475
			516 Btu		0.503 lbs

The heat liberated per pound of CO_2 absorbed $= \dfrac{516}{0.503} = 1020$ Btu/lb of CO_2. This amounts to 102 Btu per man-hour.

Hazard

The toxic properties of Baralyme are contributed from the barium hydroxide and the barium carbonate which is formed. Irritation is caused by the caustic hydroxide ion. The wetting agent in the formulation is added to eliminate dusting and therefore control airborne irritants.

Use

Baralyme should be used with a blower system. As with other absorbents, flow rates and sizing depend upon the number of people in the shelter. Theoretically two pounds of Baralyme will absorb one pound of CO_2; however, experience has shown that three pounds are needed to absorb one pound of CO_2. (Ref. 49)

The Thomas A. Edison Industries recommends using 10-1/2 lbs per man-day. This would equal 5 pounds of Baralyme per pound of CO_2 absorbed. For a 24-hour system, 10.5 pounds of Baralyme would be required per person. This would cost $3.80 or 16 cents per man-hour for the chemical. Since a blower is also needed, the following cost must be added.

A 60-cfm hand-driven blower costs approximately $50. This will support 20 people when it is operated continuously. Thus, on the basis of a 24-hour operation, 480 man-hours would cost $25 or $0.052 per man-hour. The total cost of chemical and blower would then amount to $0.21 to $0.22 per man-hour.

Baralyme can be stored from 4 to 7 years. After that period of time, it should be replaced.

2.3.1.4 <u>Soda-Lime</u> - Soda-lime has been considered for use as a carbon dioxide absorber since 1918. Early formulations were unsatisfactory because the material would cake and not allow the gas to pass through the bed. A satisfactory formulation of 90 per cent lime and 4 per cent NaOH (on a dry basis) was tested in 1928. (Ref. 50) The newer formulation consists of: (Ref. 51)

78.4% (by weight)	$Ca(OH)_2$
2.5	NaOH
1.2	KOH
17.0	moisture
0.8	binder
99.9%	

The principal reaction for soda-lime is

$$Ca(OH)_2 + CO_2 \xrightarrow{H_2O} CaCO_3 + H_2O_{liq.}$$
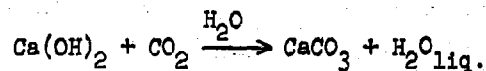
The heat of reaction at 77°F for this material is 1055 Btu per pound of CO_2 or 627 Btu per pound of calcium hydroxide. The heat liberated per man-hour is 105.

Other reactions taking place are

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O_{liq.}$$
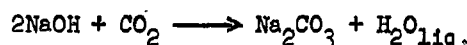
The heat of reaction at 77°F is 1710 Btu per pound of CO_2 or 945 per pound of NaOH.

If the following reaction is assumed,

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 \cdot H_2O;$$
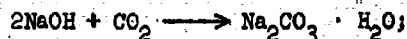
then the heat of reaction is 1800 Btu per pound of CO_2 or 990 Btu per pound of NaOH.

For $2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O_{liq}$, the heat of reaction is 1840 Btu per pound of CO_2 or 723 Btu per pound of KOH.

Constituent	Weight (%)	Btu per (lb)	Heat Liberated	lb-CO_2/lb	CO_2 Absorbed
Ca(OH)$_2$	78.4	627	490	0.594	0.465
NaOH	2.5	990*	25	0.550	0.014
KOH	1.2	723	9	0.393	0.005
Inert	17.9	---	---		-----
			524 Btu		0.484 lbs
* Assume monohydrate formation					

Heat of reaction per pound of soda-lime is 524 Btu. Because 0.484 pounds of CO_2 is absorbed for each pound of soda-lime reacted, the heat of reaction on the basis of one pound of CO_2 absorbed is 1080 Btu or 108 Btu per man-hour.

Hazards

Soda-lime has the property of forming irritating dusts. Because the material is caustic, this dust burns the eyes and mucous membranes. The dust problem has been the main reason for the rejection of soda-lime for various environment control applications although it is now used in hospitals for rebreathing apparatus.

Use

Soda-lime should be used in a blower system, although it is possible to use it by spreading it out in thin layers. When the blower system is used, it is possible to pass the scrubbed air through a filter to remove most of the soda-lime dust.

Capacity

Theoretically soda-lime if capable of absorbing 0.484 lbs of CO_2 or 2.07 pounds of soda-lime is required per pound of CO_2. A working ratio is approximaterly 3.0 pounds of soda-lime per pound of carbon dioxide.

The efficiency of the reaction is dependent upon ambient conditions. The absorption has poor efficiency below 65°F. The same is true for low relative humidities. (Ref. 52) Eight pounds of soda-lime would have to be stored for each person for 24 hours of sealed support. On the basis of a material cost of 30 cents per pound, the man-hour cost for chemicals is 9-1/2 cents. To this must be added the blower cost of 5-1/2 cents per man-hour so the total cost would be 15 cents per man-hour.

In order to store soda-lime, it must be kept in sealed containers because if it is exposed to a moist atmosphere, it will lose its capacity.

2.3.1.5 Hydroxides of Sodium, Potassium and Calcium - The solid granules or pellets of sodium, potassium or calcium hydroxide have a high theoretical capacity to absorb carbon dioxide. This capacity is not reached in an actual solid-gas absorption because the surface of the particles become covered with the carbonate which is formed and the reaction ceases.

2.3.1.6 Silver Oxide - The oxide of silver can be used to absorb carbon dioxide according to the reaction

$$Ag_2O + CO_2 \longrightarrow Ag_2CO_3$$
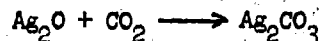
The heat liberated from this reaction is 798 Btu per pound of carbon dioxide or 151 Btu per pound of silver oxide. The silver carbonate can be regenerated by heating in the temperature range of 250 to 350°F. If the temperature exceeds this, the silver oxide will decompose to metallic silver and oxygen.

The theoretical capacity of silver oxide is 0.19 pounds of carbon dioxide per pound of Ag_2O. On this basis 0.5 pounds of Ag_2O would be required per man-hour in a nonregenerating system.

If the cost of silver oxide is $1.00 per ounce, then the cost of one man-hour of protection would be eight dollars. The cost of such a system would be prohibitive. Even in a regeneration system, the amount of Ag_2O required would be such that the cost would not be competitive with other carbon dioxide absorption methods.

2.3.2 Liquid Absorbents

Carbon dioxide can be removed from a sealed environment by absorption with solutions of hydroxides, carbonates, ethanolamines and several other chemicals.

The reactions can be carried out in four ways, which include:

1. Spreading the solution in trays so that a large surface area is exposed.

2. Bubbling carbon dioxide through a tower of solution until the absorbing chemicals are depleted and then discarding them.

3. Loading a solution as described in item 2 and then switching to a second tower while the first tower is regenerated with heat.

4. Continuously absorb and regenerate in a two-tower process.

In general, the reaction of carbon dioxide and a hydroxide takes place at a faster rate and liberates more heat than the reaction of carbon dioxide and carbonates. Thus, the hydroxides would be more suitable for passive systems or system where the solution is reacted until depletion. Likewise the reaction of the carbonate and carbon dioxide is more suitable for a regeneration system because less heat is needed to decompose the bicarbonate.

2.3.2.1 <u>Alkali Hydroxide Solutions</u> - The reactions of carbon dioxide and strong bases in solutions is basically the same as the reaction for hydroxide in the solid state; however, the reaction in solution has the following two advantages over the solid-gas reaction.

1. The reaction will not be hindered by the formation of carbonates. In the solid-state, the formation of carbonates on the surface of the hydroxide, decreases the available surface area for the absorption to take place.

2. In solutions, the carbonates will react with additional carbon dioxide to form bicarbonates. This reaction probably does not take place in the solid-gas reaction.

The following reactions can take place in solution:

$$2NaOH_{soln.} + CO_2 \longrightarrow Na_2CO_{3\,soln.} + H_2O + 47,200 \text{ Btu}$$
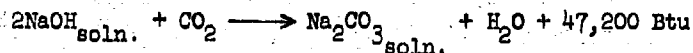
This amounts to 1070 Btu per pound of carbon dioxide or 107 Btu per man-hour.

The sodium carbonate produced can then further react with carbon dioxide to form sodium bicarbonate.

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3 + 14000 \text{ Btu}.$$
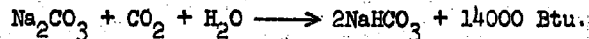
This is equal to 319 Btu per pound of CO_2 or 31.9 Btu per man-hour.

For potassium hydroxide the reactions are:

$$2KOH_{soln.} + CO_2 \longrightarrow K_2CO_{3\,soln.} + H_2O + 46,200 \text{ Btu}$$
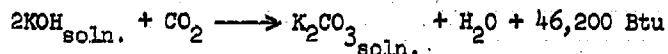
This is equivalent to 1050 Btu per pound of CO_2 or 105 Btu per man-hour.

The carbonate then reacts to form a bicarbonate.

$$K_2CO_3 + H_2O \longrightarrow 2KHCO_3 + 13,300 \text{ Btu}$$
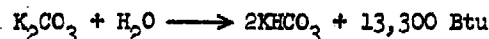
This amounts to 303 Btu per pound of CO_2 or 30.3 Btu per man-hour.

The heat of reaction indicated for the above reactions are based on very dilute solutions. Concentrations which would actually be used would be higher and thus have a slightly different heat of reaction.

The high temperature which is required to decompose sodium or potassium carbonate limits the use of alkali metal hydroxides to nonregenerative systems. This is not a serious disadvantage since the materials are cheap enough to warrant storing them in large quantities.

Temperature of Decomposition of Carbonates to Hydroxides or Oxide (Ref. 53)

Compound	Temperature, °F
Na_2CO_3	1290
K_2CO_3	1340

Hazards

The hazards involved in using solutions of hydroxides result from the caustic nature of the material. The solution will cause burns if it comes in contact with the skin. The hydroxides will also react vigorously with strong acids.

Solutions eliminate the problem of irritation from dust, but if the carbon dioxide-laden air is passed through a column at a high velocity, entrainment may become troublesome. This can largely be taken care of by entrainment separators.

Capacity

Assuming the hydroxide reacts to form the carbonate according to the reactions:

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O \qquad \text{or}$$

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O \; ,$$

the following quantities of hydroxide would be required.

Material	$\dfrac{\text{lb of } CO_2 \text{ absorbed}}{\text{lb of hydroxide}}$	$\dfrac{\text{lb of hydroxide reacted}}{\text{lb of } CO_2}$
NaOH	0.55	1.82
KOH	0.39	2.54

Assuming carbon dioxide is produced at a rate of 0.1 pounds per man-hour, 0.182 pound of NaOH or 0.254 pounds of KOH would be required per man-hour.

Tepe and Dodge (Ref. 54) found that the rate of CO_2 absorption in NaOH solution increased with an increase in hydroxide concentration up to a 2N solution. Further increases in concentration decreased the rate of absorption.
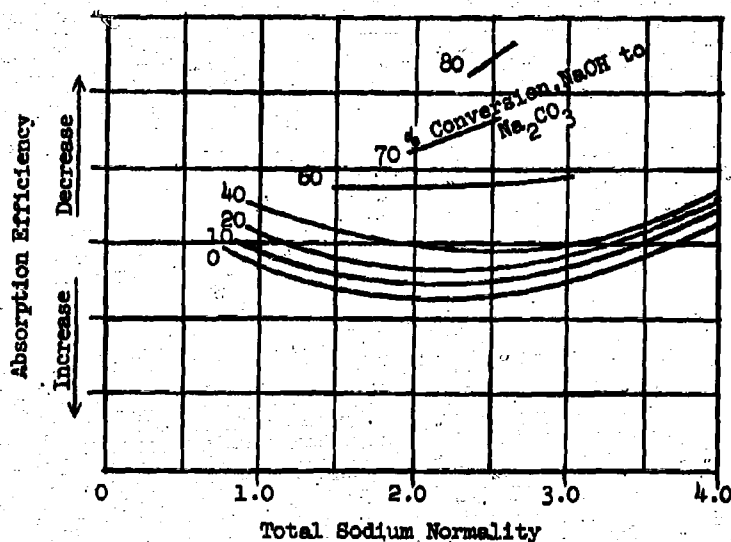
Figure 12. ABSORPTION OF CO_2 IN AQUEOUS NaOH SOLUTIONS

A 2 Normal NaOH solution contains 0.93 pounds NaOH per gallon, so approximately 5 gallons of solution would have to be stored for each person for a 24-hour closed environment.

If KOH were used, approximately 20 gallons of 2N solution would have to be stored per person since a 2N solution contains 0.67 pounds per gallon.

The cost of NaOH is $0.065-$0.08 per pound and that of KOH is $0.105 to $0.12 per pound. The cost of stored chemicals would therefore be $0.72 for NaOH or $1.45 for KOH. This equals 1.5 cents per man-hour for NaOH or 3 cents per man-hour for KOH.

The only necessary equipment for the process is a hand blower to bubble the gas through the solution and a container. No auxiliary power is required.

The predominate features of alkali metal hydroxides are:

1. low chemical cost

2. high rate of absorption

3. no power requirement.

2.3.2.2 <u>Alkaline Earth Hydroxides</u> - The alkaline earth hydroxides consist of $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$.

Most of these compounds are insoluble or are very slightly soluble in water. Calcium hydroxide is soluble up to 0.025 gram moles per liter at 32°F and barium hydroxide octohydrate is soluble up to 0.17 gram moles per liter at 50°F. All of the other alkaline solutions are less soluble than these two. The low solubilities of all the compounds in this group make their use impractical in solutions.

2.3.2.3 <u>Alkali Carbonates</u> - Solutions of alkali carbonates react with carbon dioxide and form the corresponding bicarbonates. Either sodium or potassium carbonates are practical from the consideration of solubility and cost. The reactions can be written as:

$$Na_2CO_{3_{soln.}} + CO_2 + H_2O \longrightarrow 2NaHCO_{3_{soln.}}$$

or

$$K_2CO_{3_{soln.}} + CO_2 + H_2O \longrightarrow 2KHCO_{3_{soln.}}$$
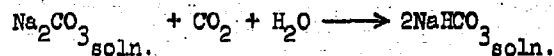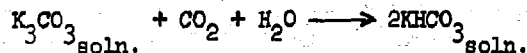
As mentioned in Section 2.3.2.1, the heat of reaction for these equations amounts to 319 Btu per pound of carbon dioxide, or 32 Btu per man-hour for the sodium carbonate, and 303 Btu per pound of carbon dioxide, or 30 Btu per man-hour for the potassium carbonate.

The use of carbonate solution for carbon dioxide absorption in a non-regenerative system is not as efficient as hydroxide solutions because the rate of reaction is less, the capacity on a pound basis is less, a larger volume of solution is needed and as the bicarbonate is formed, (see Figure 13) the reaction rate decreases. The solutions of carbonates are suitable for a regenerative system whereas the hydroxides are not.

The equilibrium is controlled by the temperature. A low temperature shifts the equilibrium toward the bicarbonate formation and a high temperature shifts the equilibrium toward the carbonate formation.
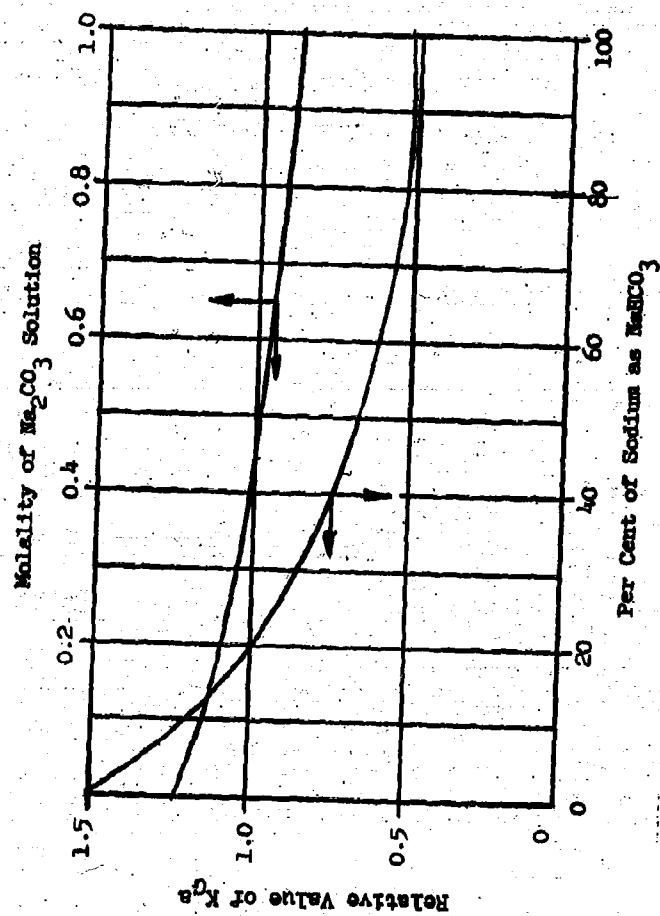
Figure 13 EFFECT OF Na_2CO_3 AND $NaHCO_3$ (Ref. 55)
CONCENTRATIONS ON RATES OF
CONVERSION

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The concentrations used for carbon dioxide absorption are approximately 1 Normal solution for Na_2CO_3 and up to 2N solution for K_2CO_3. This is equivalent to 3.3 pounds of Na_2CO_3, or 8.62 pounds of K_2CO_3 per cubic foot of solution. The capacity of Na_2CO_3 is 0.415 pounds of carbon dioxide absorbed per pound of Na_2CO_3 reacted, or 1.37 pounds of carbon dioxide absorbed per cubic foot of Na_2CO_3 solution reacted. For potassium carbonate the capacities are 0.314 pounds of carbon dioxide per pound of K_2CO_3 reacted, or 2.74 pounds of carbon dioxide per cubic foot of solution.

The following quantities of carbonate must be reacted and regenerated per man-hour.

Solution	Concentration	Rate
Na_2CO_3	1N	0.073 cubic foot/man-hr
K_2CO_3	2N	0.0365 cubic foot/man-hr

Hazards

Both sodium or potassium carbonate solution are nonhazardous unless taken internally. They are nonflammable. Carbonates will liberate carbon dioxide if they come in contact with acids. There is no reaction with bases.

Costs

The cost of the chemicals is fairly low. Sodium carbonate is approximately $0.03 per pound and potassium carbonate is $0.085 to $0.0955 per pound. In a regenerative process, this would be very small when compared to the vessels, pumps and heating and cooling apparatus.

2.3.2.4 Ethanolamines - With the development of the nuclear submarine, the need for an efficient carbon dioxide scrubber became a necessity for long underwater voyages. Caustic solutions are efficient scrubbers, but they are non-regenerable so the quantity of caustic required for the entire voyage must be carried onboard. Ethanolamines absorb carbon dioxide and are easily regenerated; however, the material undergoes oxidation with use and must be replaced periodically.

There are three ethanolamines; each of which is capable of absorbing CO_2 and then releasing it upon heating.

Compound	Molecular Weight	B. P., °F	M. P., °F
Monoethanolamine	61.1	342	50.9
Diethanolamine	105.1	511	82.4
Triethanolamine	149.2	532	70.2

The reaction of ethanolamines and carbon dioxide in the presence of water can be written as:

$$HO\ CH_2CH_2NH_2 + H_2O + CO_2 \longrightarrow HO\ CH_2CH_2NH_3^+\ HCO_3^-$$

$$(HO\ CH_2CH_2)_2NH + H_2O + CO_2 \longrightarrow (HO\ CH_2CH_2)_2NH_2^+\ HCO_3^-$$

$$(HO\ CH_2CH_3N + H_2O + CO_2 \longrightarrow (HO\ CH_2CH_2)_3NH^+\ HCO_3^-$$
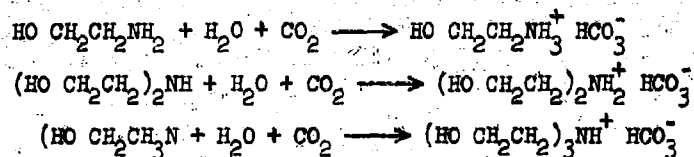
The rate of the above reactions proceed to the right (absorption) for decreasing temperatures and to the left (regeneration) for increasing temperatures.

The absorption is carried out at 100°F, then the spent solution enters the regenerator where desorption takes place from 250 to 300°F. The maximum theoretical capacity for the absorption reaction is one mole of carbon dioxide absorbed per mole of amine; (Ref. 56) however, the actual working capacity is dependent upon the partial pressure of the CO_2 in air, the temperature and the concentration of the amine.

The following table illustrates typical values for various concentrations and temperatures of ethanolamines and partial pressures of CO_2.

TABLE 10 (Ref. 57)

THE EFFECT ON ETHANOLAMINE CONCENTRATION OR TEMPERATURE
UPON THE ABSORPTION OF CARBON DIOXIDE

Compounds	Amine Normality	Temperature °F	pp of CO_2 mm Hg	$\dfrac{\text{Moles } CO_2}{\text{Moles amine}}$
MEA	0.5	32	10.6	0.675
MEA	0.5	77	10.8	0.607
MEA	2.0	32	11.4	0.601
MEA	2.0	77	10.6	0.527
MEA	2.0	122	10.1	0.489
MEA	5.0	32	11.5	0.600
MEA	5.0	77	10.6	0.507
MEA	5.0	122	10.4	0.453
MEA	9.5	32	11.4	0.538
MEA	9.5	77	11.1	0.495
MEA	9.5	122	10.8	0.443
MEA	12.5	122	10.9	0.467

TABLE 10 (Continued)

Compounds	Amine Normality	Temperature °F	pp of CO_2 mm Hg	Moles CO_2 / Moles amine
DEA	0.5	32	11.0	0.741
DEA	0.5	77	11.0	0.551
DEA	0.5	122	10.1	0.336
DEA	2.0	32	11.5	0.604
DEA	2.0	77	10.5	0.451
DEA	2.0	122	10.2	0.302
DEA	5.0	32	11.4	0.526
DEA	5.0	122	10.4	0.254
DEA	8.0	122	10.6	0.250
TEA	0.5	32	10.7	0.378
TEA	0.5	77	10.5	0.191
TEA	0.5	122	8.3	0.081
TEA	1.0	77	10.8	0.161
TEA	2.0	32	10.7	0.263
TEA	2.0	77	11.0	0.093
TEA	2.0	122	9.4	0.035
TEA	3.5	77	10.0	0.062
TEA	5.0	77	10.6	0.029

From the above table, one can see that approximately one-half mole of carbon dioxide is absorbed for each mole of amine if the level of CO_2 in the air is kept at 1.5 per cent or below. Using this assumption, ethanolamines would have the following capacities:

Compounds	lb CO_2 / lb amine	lb of amine / lb of CO_2
MEA	0.361	2.77
DEA	0.209	4.78
TEA	0.148	6.77

If the material is used in a nonregenerative system, the following quantities and costs for chemicals would be involved.

Substance	Consumption lb/man-hr	Cost $/lb	Cost $/man-hr
MEA	0.277	0.29	0.08
DEA	0.478	0.285	0.136
TEA	0.677	0.245	0.166

The quantities needed in a regenerative system would depend on the temperatures, equipment size, flow rates and quantities of antioxidant used. Since ethanolamines are subject to decomposition and oxidation, they would have to be replaced after a certain length of time in a regenerative system. The decomposition can be somewhat retarded by using stabilizers such as copper sulfate.

Hazards

The maximum acceptable concentration of any of the ethanolamines has been set at 1 part per million. (Ref. 58) The scrubbed air must therefore be filtered to insure that there are no traces of ethanolamines in it. Because ethanolamines are basic compounds, a scrubber of an acid solution removes the ethanolamines. Solutions of ethanolamines also have a tendency to foam and are somewhat corrosive.

2.3.2.5 Alkazid M - Alkazid M is the potassium salt of the amino acid N-methylalanine.

$$CH_3 \diagdown \!\!\!\!\!\! {\underset{H}{N}} \!\!-\!\! \overset{H}{\underset{CH_3}{C}} \!\!-\!\! C \overset{O}{\underset{O^-\ K^+}{\diagup}}$$
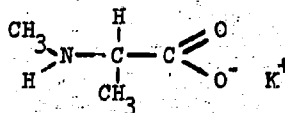
molecular weight - 141

Alkazid M is believed to be much more expensive and may be in limited supply since the only known manufacturer is in Europe.

2.3.2.6 Sulfate Process - The electrolytic sulfate process absorbs CO_2 from the atmosphere. The description of this system is found in Section 2.2.2.5.

2.3.2.7 Absorption with Water - Water absorbs carbon dioxide from the atmosphere in a greater quantity than it absorbs the other constituents of the air. Therefore it can be used to separate the carbon dioxide from oxygen and nitrogen. This method of carbon dioxide absorption can either be used batchwise or in a continuous process. Regeneration can be easily accomplished by heating since the equilibrium capacity is a function of temperature and the partial pressure of CO_2 in the gaseous phase.

The amount of carbon dioxide which water is capable of absorbing can be calculated from Henry's law.

$$H = \frac{p_{CO_2}}{X_{CO_2}}$$

where H =   Henry's constant

    p =   partial pressure of CO_2 in the atmosphere

    X =   mole fraction of CO_2 in solution

For the system carbon dioxide and water, Henry's constant has the following values for various temperatures. (Ref. 59)

Temperature, °F	H
32	728
41	876
50	1040
59	1220
68	1420
77	1640
86	1860
95	2090
104	2330
113	2570
122	2830
140	3410

Assuming a maximum carbon dioxide concentration of 1-1/2% or 0.015 atm. and a temperature of 77°F, the following quantity of water would be required to absorb 1 lb of carbon dioxide.

From the above table

    H =   1640 atm.

    p =   0.015 atm.

    X = $\frac{p}{H}$ = 9.16 x 10^{-6}

    f_a =   weight fraction CO_2

    f_b =   weight fraction water

    M_a =   molecular weight of CO_2

    M_b =   molecular weight of water

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$$X = \frac{f_a/M_b}{f_a/M_a + f_b/M_b}$$

$$X = \frac{f_a/M_a}{f_a/M_a + (1 - f_a)/M_b}$$

$$9.16 \times 10^{-6} = \frac{f_a/44}{f_a/44 + (1-f_a)/18}$$

$$f_a = 2.24 \times 10^{-4} \frac{lb\ CO_2}{lb\ H_2O}$$

Because carbon dioxide is produced at a rate of 0.1 pounds per man-hour, water for absorption must be furnished at a rate of 447 pounds per man-hour. This is equal to 53.5 gallons per man-hour.

Hazards

There are no hazards involved in this system insofar as toxic materials are concerned.

Although the use of water without additional chemical constituents would absorb carbon dioxide and provide an emergency supply of drinking water, the volume and equipment necessary make this process impractical. If water is used without regeneration, 1300 gallons would be needed per person for 24 hours. This would occupy 165 cubic feet per person.

If regeneration is used, 447 pounds of water per man-hour would have to be heated from 70°F to approximately 200°F for regeneration and then refrigerated for absorption.

2.3.3 Carbon Dioxide Adsorption

Carbon dioxide can be adsorbed on the surface of certain porous solids which have a large surface area in proportion to their weight. These substances are easily regenerated because the bonding is a function of physical properties rather than chemical properties.

2.3.3.1 Molecular Sieves - Molecular Sieves are synthetic zeolites made by the Linde Company. They have an affinity for certain molecules which they trap in their pores. Among these are water, hydrocarbons and carbon dioxide. The capacity of carbon dioxide is dependent upon the partial pressure and the temperature of the carbon dioxide in the air to be scrubbed. Below is a diagram showing capacity as a function of partial pressure at 77°F.

Carbon Dioxide Partial Pressure, mm of Hg
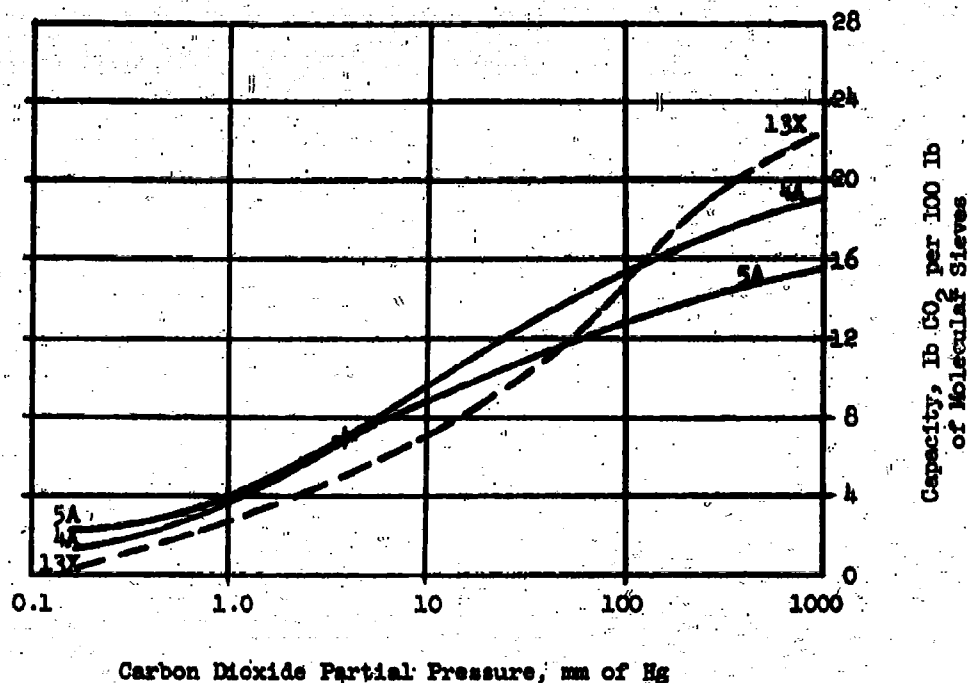
Figure 14   CAPACITY OF MOLECULAR SIEVES AT 70°F (Ref. 60)

If the carbon dioxide level is maintained at 1-1/2% the following amounts
of adsorbent are required.

Sieve Type	Capacity $\dfrac{\text{lb } CO_2}{100 \text{ lb adsorbent}}$
4A	9.0
5A	9.3
13X	7.4

Heat of Reaction

The heat of adsorption for carbon dioxide is much lower than heat of
adsorption of CO_2 with caustic solutions. The heat of adsorption is 300 Btu
per pound of carbon dioxide or 30 Btu per man-hour.

Special Requirement

Before the air from the environment is passed through the bed of Molecular Sieves it must be completely dry because Molecular Sieves have a greater affinity for water than they do for carbon dioxide. This can be accomplished by first passing air through a bed of desiccant such as silica gel.

If Molecular Sieves are used without regeneration in a simple batch process, approximately 1.1 pounds of Type 5A sieve would be required per man-hour. Because of the high cost (about $1.55/lb) a nonregenerative system is not practical from a cost comparison.

Molecular Sieves loaded with carbon dioxide are regenerated at room temperature by applying a vacuum to the bed. A cooling period is not required because it is not necessary to heat the bed. Therefore if the cycle is changed from adsorption to regeneration every hour, 1.1 pounds will be required per person for the regeneration unit.

2.3.3.2 Other Adsorbents - Other substances which will adsorb carbon dioxide from a dry atmosphere are silica gel, activated alumina and activated carbon. The capacity of these adsorbents is less than Molecular Sieves by a factor of 5 to 10. At a partial pressure of 11.4 mm Hg or 1-1/2% CO_2, and a temperature of 77°F, the adsorbents have the following capacities.

Adsorbent	Capacity $\dfrac{lb\ CO_2}{100\ lb\ adsorbent}$ (Ref. 61)
Silica Gel	2.2
Activated Alumina	1.0
Activated Carbon	0.8

Based on the above values, the following quantities would be used per man-hour.

Adsorbent	Rate used $\dfrac{lb}{man\text{-}hour}$
Silica Gel	4.5
Activated Alumina	10
Activated Carbon	12.5

The material is used then in the same manner as the Molecular Sieves described in Section 2.3.3.1. The following quantities would be required per person if the cycle is reversed every hour.

Adsorbent	Quantity
Silica Gel	9.0 lbs
Activated Alumina	20
Activated Carbon	25

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Silica gel and activated alumina have a greater affinity for water than they do for carbon dioxide so that the entering air must pass through a bed of desiccant before passing through the bed of carbon dioxide adsorbent.

2.3.4 Mechanical Carbon Dioxide Removal

2.3.4.1 Freeze-Out Technique - Carbon dioxide may be removed from air in a manner similar to that of removing moisture from air by dehumidification. The air is cooled until the dew point of the carbon dioxide is reached. Further cooling results in the separation of the carbon dioxide in the form of solid crystals. If the air contains 1-1/2 per cent carbon dioxide, the carbon dioxide will not begin to precipitate until -185°F. To remove 90 per cent of the carbon dioxide the temperature will have to be further reduced to -212°F.

The amount of refrigeration needed to carry out such an operation would be impractical when more simple scrubbing methods are available. Also a power loss would result in a shut-down of the equipment.

2.3.4.2 Diffusion Methods - Gases will diffuse through a membrane at different rates so that a separation will take place and concentrations will change. The following table lists the relative diffusion rates of various gases through rubber. (Ref. 62)

Gas	Relative Rate
Nitrogen	1.0 (basis)
Acetylene	0.85
Carbon dioxide	13.7
Oxygen	2.29

When natural rubber is used as the membrane, approximately 1100 square feet of surface area are required to diffuse 0.1 lb of CO_2 per hour per person. At the same time some of the oxygen would be lost.

The large surface area required makes this method impractical at the present time.

2.3.5 Comparison of Various Carbon Dioxide Removal Systems

The following table is a comparison of carbon dioxide removal systems.

TABLE 11

COMPARISON OF SYSTEMS

Type	Reliability	Power Requirement	Cost/man-hr	Storage Handling	Heat Liberated Btu/man-hr
Lithium Hydroxide	Good	None	$0.48	Fair-Good	130
Baralyme	Good	Manual	0.12-0.48	Fair-Good	100
Soda-lime	Good	Manual	0.10	Fair-Good	105
Sodium or Potassium Hydroxide	Fair	None	Low	Fair	140
Silver Oxide	Good	None	8.00	Good	80
Alkali Hydroxide sol.	Good	Manual	0.18-0.25	Fair	107
Alkali Carbonates	Fair	Manual	0.24-0.33	Good	30
Ethanolamines	Fair	Manual	0.28-0.68	Poor-Fair	
Alkazid M	Fair	Manual	High	Unknown	
Water	Fair	Manual	Low	Good	
Molecular Sieve	Fair	Manual	1.55	Good	30
Silica Gel	Fair	Manual	Moderate	Good	
Activated Alumina	Fair	Manual	1.20	Good	
Activated Carbon	Fair	Manual	High	Good	
Freeze-out	Fair	Very High	High	Fair	
Diffusion	Fair	Manual	High	Fair	

Removal of carbon dioxide can be accomplished with either a solid-gas reaction, liquid-gas reaction or adsorption.

Reliability

Solids - Lithium hydroxide, Baralyme and soda-lime have all been used to control the CO_2 level aboard submarines. Silver oxide has been suggested as a regenerable absorbent for carbon dioxide in space vehicles. Potassium and sodium hydroxide have a good theoretical capacity, however the formation of surface carbonates hinder the reaction.

Solutions - Alkali hydroxide solutions are the most reliable of the various solutions considered. They are used industrially and for submarine service. Alkali carbonates are usable but they do not have as rapid a rate of reaction as do the hydroxides. Ethanolamines are used for carbon dioxide scrubbing however they are subject to oxidation and have a tendency to foam. The reliability of Alkazid M is not known at this time since this chemical is not widely available in this country. Water has only fair reliability because an increase in water temperature will decrease the capacity of the process.

Adsorbents - Molecular Sieves, activated alumina, and silica gel have a preference of water over carbon dioxide; thus any trace of moisture reaching the bed would drive off the previously adsorbed CO_2 and prevent further CO_2 adsorption. Activated carbon will adsorb high molecular weight compounds in preference to carbon dioxide so this adsorbent can be poisoned by contaminants with the shelter.

Mechanical Methods - The reliability of freeze-out techniques is dependent upon the reliability of the power supply for the refrigerator. Diffusion is of questionable reliability since this is not a commonly used method and a puncture of the membrane would ruin the operation.

Power Requirements

Solid Absorbents - Solid absorbents can be used without a forced air system; however if a manual blower is available the efficiency of absorption will be increased.

Liquid Absorbents - A manual blower is needed in a liquid system in order to bubble the air through the solution. Additional power is required in a regenerable system for heating and cooling.

Adsorbents - Adsorbents require a blower to move the air through the bed of granules and if regeneration is used, a method of heating and cooling is also required.

Mechanical Methods - The freeze-out method requires a large amount of power for refrigeration while the diffusion method requires only a blower.

Costs

The cost of the chemicals for carbon dioxide on a man-hour basis were shown in Table 11. These costs are based on a nonregenerative system. Where regeneration is used, a smaller investment is needed for chemicals; however, the investment in equipment is greater.

Storage and Handling

Solid Absorbents - All of the solid absorbents consist of caustic materials which should not be handled directly with moist hands. The alkali hydroxides are especially irritating in this manner. Dusting is another problem encountered with this type of absorbent; however, manufacturing techniques are helping to overcome this problem.

The shelf life should be indefinite as long as the material is kept sealed; however the manufacturers of Baralyme recommended a storage period of not longer than 4 years. Soda-lime probably is not storable for periods of time longer than this.

Liquids - Alkali hydroxide solutions must be stored in suitable containers and all contact with the skin must be avoided. Alkali carbonates are also caustic but contact with the skin is not as serious a problem. Ethanolamines will not affect the skin of most persons for a short contact however, the vapor of these compounds are hazardous in concentrations greater than 1 ppm. Alkazid M is much less toxic than the ethanolamines and has less problems when it is used. Water presents no problems except the storage of a very large quantity of liquid.

Adsorbents - The solids which remove carbon dioxide by adsorption have good shelf life as long as they are kept sealed and moisture-free. Handling is simple because the material would already be in its canister. Thus one would uncap the ports and hook-up a blower.

Mechanical Method - Mechanical methods present no problems of storage or handling.

Of the various carbon dioxide absorbents, the following will be subjected to further evaluation. Lithium hydroxide, Baralyme, and Soda-lime will be compared to determine the best solid absorbent at a reasonable cost.

Other absorbents will no longer be considered because of high cost, low capacity, unreliability or toxicity.

2.4 Odor and Contaminant Control

Within a sealed environment, there exists a possibility of toxic and noxious materials accumulating and producing adverse effects upon the habitants of the shelter. These substances come from both equipment and humans. Fuels, lubricants, and oils produce various hydrocarbons; refrigerants produce Freons and electrical discharges produce ozone. The human body will produce esters and fatty acids from perspiration, ammonia from urine, and hydrogen sulfide, ammonia, phenols, indoles, skatoles, mercaptans from feces and flatus. Odors can also come from food preparation or decay of garbage. Partial oxidation of certain compounds will convert a low odor chemical to a high odor compound. An example of this is shown below.

Butanol	-	Low odor
Butyaldehyde	-	High odor
Butyric acid	-	Very high odor

Table 13 is a list of the permissible levels of various compounds which could be found in a sealed shelter. These values are based on an eight-hour industrial work day. The fact that these are values for an eight-hour exposure instead of a continuous exposure is somewhat corrected by the fact that they are based on an indefinite number of working days whereas the confinement in the shelter probably would not be more than one day without ventilation.

Where the different authors give the same value, one number is listed in the table. Where there is a disagreement, all the values are given.

These chemicals can be removed by adsorption on porous materials having a large surface area such as activated carbon or Molecular Sieves, absorption such as the removal of the acid gases by the carbon dioxide absorbent, or combustion promoted with catalysts. Another industrial method is the use of masking odors to cover up the obnoxious odors, but since this does not remove the contaminant it will not be given further consideration.

2.4.1 Activated Carbon

Activated carbon has been used since World War I to adsorb poisonous and obnoxious gases. Activated carbon will adsorb practically all organic chemicals except those of low molecular weight. It will also adsorb certain inorganic materials. Generally, the attraction for adsorption increases with an increase in boiling point and/or an increase in molecular weight.

Since the removal of contaminants from the air takes place by physical attraction rather than chemical reaction, the heat of adsorption is much less than the heat evolved from chemical absorption.

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TABLE 12   (Refs. 63, 64 and 65)

PERMISSIBLE LEVELS OF VARIOUS COMPOUNDS IN AIR

Substance	MAC*, ppm	Substance	MAC, ppm
Ammonia	100	Gasoline	500
Carbon dioxide	5000	Toluene	200
Carbon monoxide	100	Xylene	200
Carbon tetrachloride	25-50	Benzene	35-100
$C\ Cl_2F_2$	100,000	Formaldehyde	5-10
Hydrogen Chloride	5, 10	Ozone	0.1-0.05
Hydrogen Fluoride	3	Fluorine	3
Hydrogen Sulfide	20	Mercury	0.1 mg/m^3-0.1 g/
Methane	10,000	Areolein	0.5
CH_3Br	20	Stibine	0.1
CH_2BrCl	40	Phosgene	1
NO_2	5, 25	Amylacetate	200
NO	25	Butyl acetate	200
N_2O_3	25	Carbon bisulfide	20
Phenol	5	Dichloroethylether	15
Chlorine	1	Ether	400
Freon 12	1,000	Ethyl acetate	400
Ethanol	1,000	Ethylene dichloride	100
Methanol	200	Hydrogen cyanide	20
Freon 114	1,000	Methyl chloride	100
Trichloroethylene	200	Styrene	400
		Sulfur dioxide	10

*Maximum Allowable Concentration

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Some of the chemicals which activated carbon adsorbs are listed in Table 13.

TABLE 13 (Ref. 66)

ADSORPTION CAPACITY OF ACTIVATED CARBON

Substance	Dynamic Capacity ($\frac{\text{wt. of gas}}{\text{wt. of carbon}}$ x 100)
Butyric acid	40%
Valeric acid	40
Indole	25
Skatole	25
Sewer odors	High
Toilet odors	High
Chloroform	40
Carbon Tetrachloride	45
Indoform	30
Pyridine	25
Nicotine	25
Nitrobenzene	20
Putrescine	25
Body odor	High
Cooking odor	High
Raw food odor	High
Chlorine	15
Bromine	40
Iodine	40
Hydrofluoric acid	10
Hydrochloric acid	12
Hydrobromic acid	12
Nitrogen dioxide	10
Nitric acid	20
Propane	5
Butane	8
Pentane	12

TABLE 13 (Continued)

Substance	Dynamic Capacity ($\frac{\text{wt. of gas}}{\text{wt. of carbon}} \times 100$)
Hexane	16
Heptane	23
Octane, nonane or decane	25
Acetylene	2
Butyne	8
Ethylene	3
Propylene	5
Pentalene	12
Benzene	25
Toluene	29
Xylene	34
Turpentine	32
Naphthalene	30
Methanol	10
Ethanol	21
Isopropanol	26
Butyl alcohol	30
Amyl alcohol	35
Methyl ether	10
Ethyl ether	15
Isopropyl ether	18
Butyl ether	20
Methyl mercaptan	20
Ethyl mercaptan	23
Propyl mercaptan	25
Carbon bisulfide	15
Sulfur dioxide	10
Sulfur trioxide	15
Cresol	30
Menthol	30

TABLE 13 (Continued)

Substance	Dynamic Capacity ($\frac{\text{wt. of gas}}{\text{wt. of carbon}}$ x 100)
Formaldehyde	3
Acetaldehyde	7
Butyraldehyde	21
Acryaldehyde	15
Crotonaldehyde	30
Formic acid	7
Acetic acid	40
Propionic acid	40
Acrylic acid	20
Caprylic acid	35
Lactic acid	30
Methyl acetate	16
Ethyl acetate	19
Isopropyl acetate	23
Amyl acetate	34
Butyl acetate	28
Acetone	15
Methyl ethyl ketone	25
Diethyl ketone	30
Methyl isobutyl ketone	30
Encalyptole	20
Camphor	20
Essential oils	High
Methyl Chloride	5
Ethyl Chloride	12
Isopropyl chloride	20
Butyl chloride	25
Methylene chloride	25
Sulfuric acid	30
Hydrogen sulfide	3
Water	Low

Activated carbon is best used dynamically in a bed or canister wtih air circulated through it by means of a blower. This arrangement forces most of the air to eventually pass through the bed and thus keep the level of contaminants low. In a small shelter the activated carbon will still absorb contaminants if it is spread in trays. However, poor air circulation within the shelter would lower the effectiveness of the adsorbent. There are no hazards to health insofar as the carbon is concerned, however, it may adsorb chemicals which are toxic, thus spent adsorbent must be carefully disposed of.

The quantity of carbon needed varies with size and makeup of shelter, but from one-quarter to one-half pound per person should be sufficient for most situations. Assuming the activated charcoal costs $0.65 per pound and one-half were supplied per person, then the cost of removing odors and contaminants would be $0.33 per person. This cost does not include the cost of the blower. If the carbon bed is put in series with a carbon dioxide scrubber or other circulation equipment, an additional blower would not be needed.

2.4.2 Molecular Sieve 13X

Molecular Sieves will remove practically the same contaminants as activated carbon. Depending upon the size of the adsorption bed, a choice is available from among a powder, a 1/16 inch pellet and a 1/8 inch pellet. The Linde Company recommends that the ratio of bed diameter to pellet diameter be at least 20.

The capacity of Molecular Sieves increases with an increase of either the molecular weight or the boiling point of the adsorbate.

The following are generalizations concerning the use of Molecular Sieve 13X to remove contaminants present in air in concentrations of 1 to 5 ppm, temperatures of 68 to 90°F, and flow rate of 100 foot per minute and atmospheric pressure. (Ref. 67)

1. There is no adsorption of aliphatic hydrocarbons with three or less carbon atoms.

2. Nonpolar alphatics which have seven carbon atoms or more have a breakthrough capacity of approximately one-half to one per cent the adsorbent weight and a minimum effluent concentration of 0.5 ppm or lower until breakthrough.

3. Simple nonpolar aromatics have a breakthrough capacity of approximately 0.4 weight per cent. The minimum effluent concentration for benzene is 0.4 ppm and is 0.3 ppm for toluene.

4. Polar low molecular weight compounds such as ethanol have characteristics similar to benzene.

5.   Polar aromatics have a breakthrough capacity of approximately
     one weight per cent and a minimum effluent concentration of
     0.1 ppm until breakthrough.

     For the most part, activated carbon will adsorb the same compounds as
Molecular Sieves at a much higher capacity. Since activated carbon costs
approximately one-third as much as Molecular Sieves, and has ten to thirty
times as much capacity, there appears to be no special advantage in using
Molecular Sieves.

2.4.3 Combustion

     Combustion of contaminants reduces the organics to carbon dioxide and
water. This may be accomplished by passing the air over a flame, but this
would add unnecessary heat to the shelter, consume oxygen, and produce carbon
dioxide.

     In order to decrease the temperature at which the oxidation takes place
the combustion can be accomplished catalytically using either Hopcalite or an
inert metal such as platinum.

          2.4.3.1 Hopcalite - Hopcalite was originally developed for the U.S.
Navy during World War I to catalyze carbon monoxide to dioxide in gas masks
used aboard submarines.

     This is a coprecipitated catalyst containing equal portions of manganese
oxide and copper oxide. (Ref. 68)

     Hopcalite has the characteristics of oxidizing carbon monoxide to carbon
dioxide at room temperature, and hydrocarbons, organics or hydrogen at 650°F.
The majority of the compounds are oxidized to carbon dioxide at a conversion
of 80 to 100 per cent, while methane is converted to carbon dioxide and water
at only 5 to 20 per cent.

     Moisture will poison the catalyst at temperatures below 250°F, so that
moisture must be removed from the air before it is passed through the catalytic
bed or the reaction must be carried out above 250°F. The high temperature
reaction is preferred since at the elevated temperature, the catalyst will not
absorb hydrocarbons and form a possible explosive hazard.

     Hopcalite is manufactured by the Mine Safety Appliance Company and is used
in units of their design.

          2.4.3.2 Metal Catalysts - An example of a metal catalyst is platinum
wire or gauze which is heated to 500°F. Another method is to deposit the
platinum on ceramic rods or nickel alloys and preheat the air before passing
over the catalyst.

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The principal advantage of this type of oxidation is that the reaction is carried out at a temperature 500° to 800°F below an uncatalyzed incineration. (Ref. 69)

Heat exchangers are necessary to conserve the amount of power needed to heat the air to 500°F and prevent hot gases from passing directly into the shelter.

The primary requirement is that all of the constituents are in the gaseous state.

Catalytic methods have the disadvantage of adding to the heat load of the shelter and requiring a source of power to maintain the necessary temperature for the reaction.

2.4.4 Comparison of Contaminant Removal Systems

Reliability. Activated carbon and Molecular Sieves are reliable adsorbents which can be utilized without power at room temperature. Hopcalite and platinum are oxidation catalysts which remove carbon monoxide and low molecular weight hydrocarbons which are not adsorbed. These depend upon the reliability of the power supply to heat the air up to 500°F.

Power Requirement. The adsorbents require no power although a hand blower and canister process is more efficient than simply spreading the chemicals in trays.

A system using catalytic oxidation requires power to raise the temperature to 500°F. This must be furnished by either electrically heating the platinum wire or preheating the air with a burner such as a propane torch.

Cost. The cost of activated carbon is approximately $0.65 per pound, thus on the basis of one-half pound required per person, the investment would be about $0.33 plus the container cost.

Molecular Sieves cost approximately $2.00 per pound and remove practically the same contaminants as activated carbon.

Storage and Handling. Contaminant control chemicals present no unusual problems in handling or storage. They must be kept in sealed containers or canisters and connected to a blower when needed. The materials themselves are not hazardous but may become contaminated with toxic compounds.

The spent adsorbents should be carefully disposed of in sealed containers.

The catalytic combustion units will be built into the oxidation apparatus. In fact, Mine Safety Appliance Company only sells Hopcalite in units of their design.

2.5 Thermal Control

The temperature rise, θ_i, in underground shelter is dependent upon many factors as shown by the following equation. (Ref. 70)

$$\theta_i = \frac{q'}{Ak}\left[af(F) + \frac{k}{U'}\right], \quad F = \frac{\alpha t}{a^2}$$

where,

θ_i = air temperature increase, °F

A = total shelter surface area, ft^2

q' = steady heat input to air, Btu/hr

k = thermal conductivity of soil, Btu-ft/hr-ft^2-°F (Table 14)

a^2 = shape factor for shelter, ft^2

α = diffusivity of soil, ft^2/hr (Table 14)

t = time, hr

U' = coefficient of heat transfer between air in shelter and shelter wall, Btu/hr-ft^2-°F

The final temperature is the sum of the initial soil temperature and the temperature rise.

Figure 15 is a plot of temperature rise versus time calculated by this equation for a 10-man, 10-foot by 12-foot by 8-foot underground shelter fabricated of 3-inch concrete surrounded by three types of soils. A heat addition rate of 700 Btu/hr per person (500 Btu/hr metabolic plus 200 Btu/hr process and waste heat) is assumed. A sample calculation of the air temperature increase for a shelter surrounded by a normal silt at the end of 24 hours follows:

$$a^2 = \frac{A}{4\pi} = \frac{592 \text{ ft}^2}{4\pi} = 47 \text{ ft}^2.$$

$$F = \frac{\alpha t}{a^2} = \frac{0.0198 \text{ ft}^2/\text{hr} \times 24 \text{ hr}}{47 \text{ ft}^2} = 0.01$$

$$f(F) = 0.11$$

$$\theta_i = \frac{7000 \text{ Btu/hr}\left[6.9 \text{ ft} \times 0.11 + \dfrac{.516 \text{ Btu-ft/hr-ft}^2\text{-°F}}{0.6 \text{ Btu/hr-ft}^2\text{-°F}}\right]}{592 \text{ ft}^2 \times 0.516 \text{ Btu-ft/hr-ft}^2\text{-°F}}$$

$$= 37\text{°F (increase)}$$

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TABLE 14

THERMAL CHARACTERISTICS OF SEVERAL SOILS

DESCRIPTION AND CLASS OF SOILS	SOIL CONDITION % OF SATURATION	WET DENSITY LB/FT³ (D)	MOISTURE CONTENT % OF DRY WT (w)	DEGREE OF COMPACTION % OF MAX.	THERMAL CONDUCTIVITY BTU/HR/FT² /°F/FT (k)	SPECIFIC HEAT AT 55°F DRY SOIL BTU/LB/°F (c)	SPECIFIC HEAT OF MIXTURE AT 55°F BTU/LB /°F (Cm)	THERMAL DIFFUSIVITY $\alpha = \frac{k}{Cm}$
Silt and Clay (CL) & (ML)	Normal 50%	80	21	Loose Fill 66	0.516	0.175	0.326	0.0198
"	Wet 75%	80	30.5	"	0.591	0.175	0.368	0.0201
"	Normal 50%	120	7.5	Max. Comp. 100	0.782	0.175	0.233	0.0280
"	Wet 75%	120	11	"	0.982	0.175	0.257	0.0318
Sandy Soils (SW),(GP),(SM)	Normal 50%	90	16	Loose Fill 69	0.825	0.175	0.288	0.0319
"	Wet 75%	90	24.5	"	0.925	0.175	0.337	0.0305
"	Normal 50%	140	4	Max. Comp. 100	1.66	0.175	0.206	0.0575
"	Wet 75%	140	5.5	"	1.91	0.175	0.218	0.0626
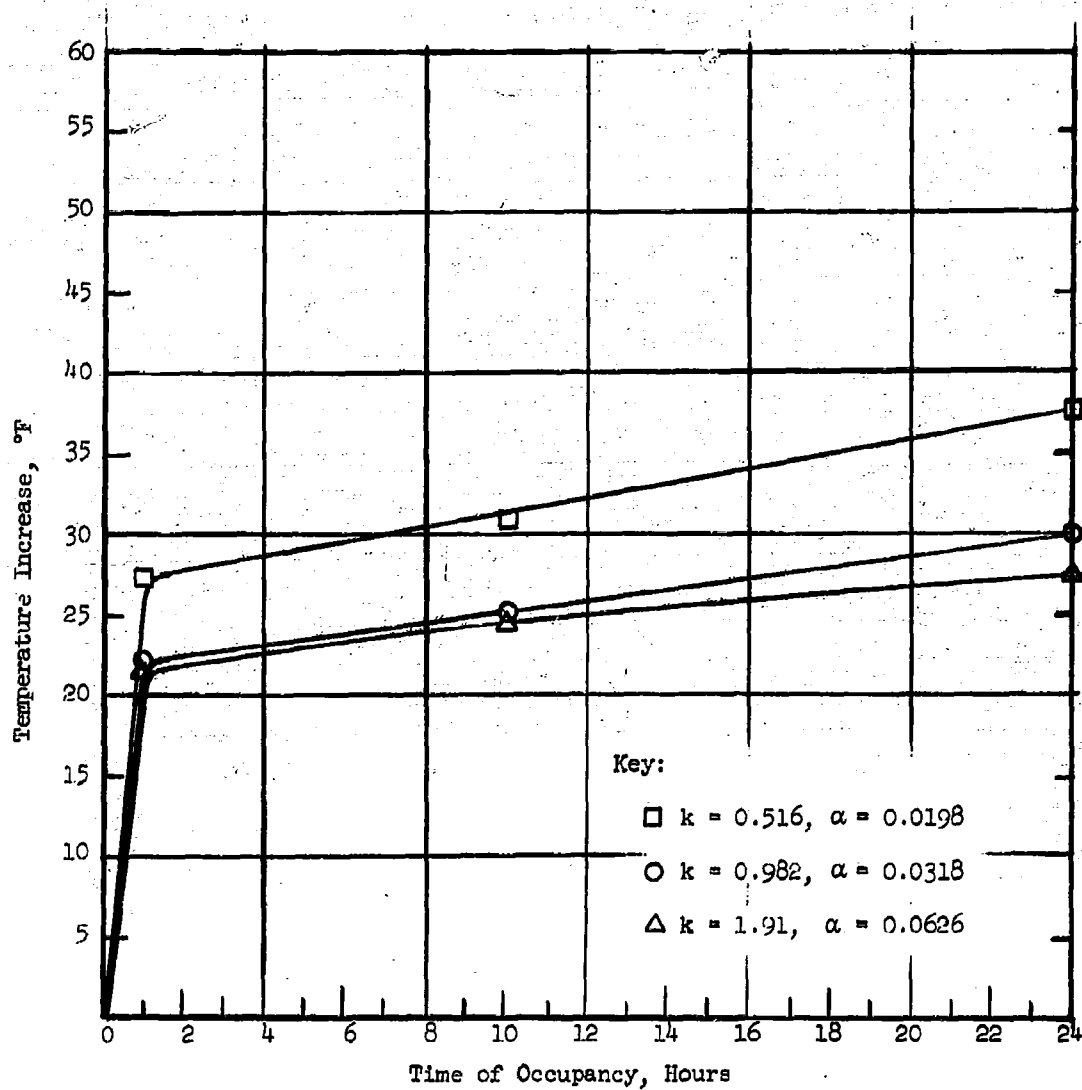
Figure 15 TEMPERATURE INCREASE IN A 10-MAN UNDERGROUND SHELTER
3 IN. CONCRETE, 10 FT x 12 FT x 8 FT, 700 BTU/HR-MAN

As shown by the Figure, unbearable air temperature may result within 24 hours, dependent upon the initial soil temperatures. The lar___ _____ers will produce even higher temperatures because of the higher heat loading per unit of wall area.

In a few isolated situations the addition of heat may be required in shelters, but in the great majority of cases both sensible and latent heat must be rejected from the shelter environment. Sensible heat may be removed from the environment by convective heat exchangers and rejected to an external sink by active refrigeration systems or miscellaneous passive systems. Latent heat may be removed from the atmosphere by mechanical condensation methods (cooling below dew point or compression until the water vapor pressure is higher than the saturation pressure), or chemical condensation methods (absorption or adsorption).

2.5.1 Heat Removal by Mechanical Process

Any surface in the shelter environment which is at a lower temperature than the shelter air will remove heat from the air. These surfaces may include spray chambers, cooling coils, or the shelter walls. Only sensible heat is transferred if the surface temperature is higher than the dew point temperature of the air, but both sensible and latent heat are removed if the surface temperature is lower than the dew point temperature.

The cycle diagram for surface cooling by a coil in which a refrigerant is circulated is shown below:

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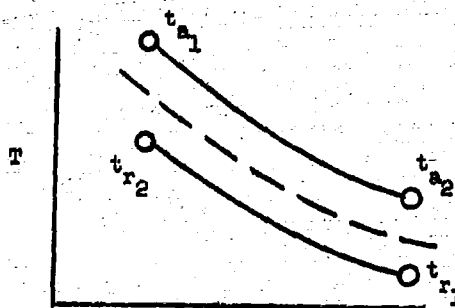
The leaving air is usually not saturated as it is in the case of a water spray chamber cycle shown below:
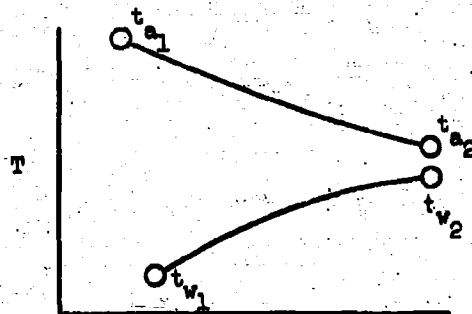
With a spray chamber the approach to 100-per-cent contacting efficiency between air and water permits the assumption of saturated leaving-air conditions. Water and air leave at approximately the same temperature, which is considered as the apparatus dew point.

The performance of a cooling surface is considerably more complicated to predict. It is basically dependent upon: (1) temperature differential between the apparatus dew point and the mean refrigerant temperature, and (2) the by-pass factor. Temperature differential, in turn, is dependent upon:

1. The design of the entire coil apparatus with respect to prime surface and extended surface in ratio and arrangement.

2. The refrigerant characteristics.

3. The refrigerant circuit arrangement with respect to refrigerant velocity and distribution.

4. The rate of loading ($Btu/hr-ft^2$).

The by-pass factor for a given coil depends on:

1. The physical form of the surface.

2. Air velocity over the surface. (The by-pass factor increases slightly as the velocity is increased.)

3. The ratio of surface area to free area in a unit depth of coil.

4. The number of units in series in the direction of the air flow.

The total heat transfer for either a spray chamber of cooling coil may be expressed as follows:

$$Q = V(1 - BF)(h_1 - h_{as})$$

where, Q = heat rejected, Btu/hr

V = air flow rate, ft^3/min

BF = by-pass factor

h_1 = enthalpy of entering air, Btu/lb

h_{as} = enthalpy of air at the apparatus dew point

To illustrate the principles previously described, the performance of a typical cooling coil is depicted on a psychometric chart below.

Dry Bulb Temperature, °F
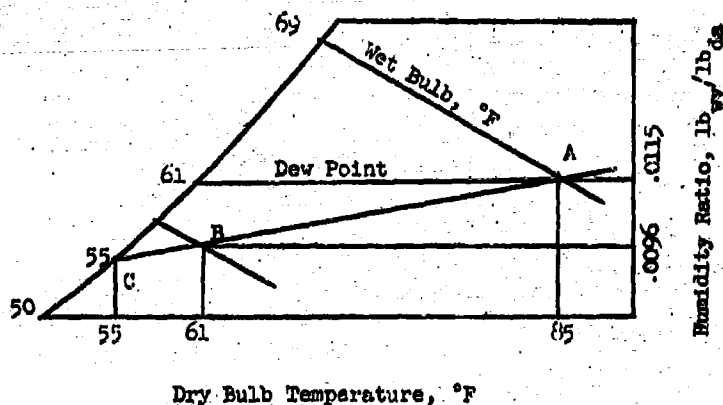
Point A represents the properties of the air entering the coil. As shown, air at a DBT of 85°F and a WBT of 69°F contains 0.0115 lb_{wv} per lb_{da}. Air with these properties can be cooled to 61°F before condensation occurs. The enthalpy of the entering air is 33.3 Btu/lb.

Point C represents the so-called apparatus dew point which is the effective surface temperature of the cooling coil when condensation is present. The DBT and WBT of the air leaving the coil, point B, is less than the apparatus dew point as shown. The ratio of the length of line BC to that of line AC represents the coil by-pass factor, which, for this example, is approximately 0.2.

The enthalpy of air leaving the coil is 25.3 Btu/lb. Therefore, 0.8 (33.3 - 25.3) or 6.4 Btu of heat are rejected for every pound of air passing through the coil. The water vapor content of the air leaving the coil is 0.0009 lb/lb_{da} so that 0.0025 lb_{wv} are removed for every pound of air passing through the coil.

2.5.2 Heat Removal by Chemical Process

Latent heat may be chemically removed (converted to sensible) from the shelter atmosphere by either absorption- or adsorption-type desiccants. The minimum amount of heat liberated during condensation of one pound of water at 77°F and 14.7 psia is 1050 Btu regardless of the method. Absorption, in which the water reacts chemically with the desiccant to form a hydrate or hydroxide, generally liberates a heat of reaction (exothermic reaction) in addition to the heat of condensation. Certain desiccants which react endothermically with water do exist, but are not practical. Adsorbents, such as silica gel, in which the water is physically attached to the surface of the material, usually liberate a much smaller amount of heat.

2.5.2.1 Typical Example - A typical exothermic dehydration cycle is depicted on the psychometric chart below:
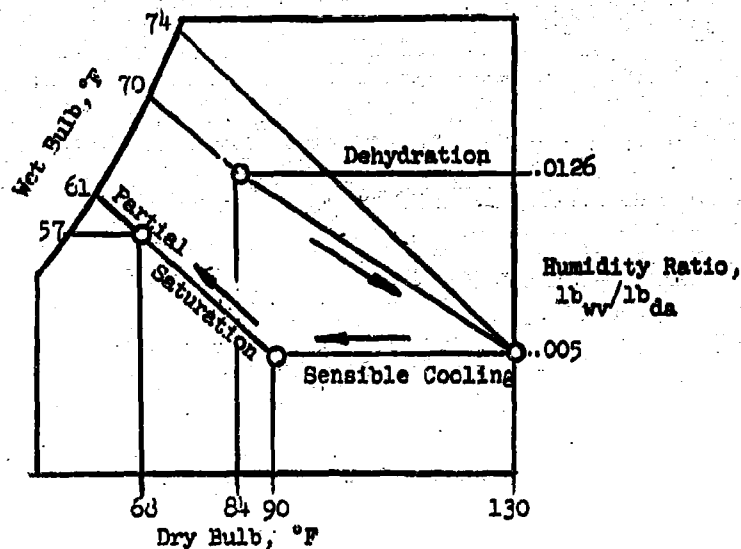
As shown, 0.121 lb_{wv} per lb_{da} are removed as air passes through the desiccant. Also, it is noted that the dry bulb temperature increases from 84°F to 130°F. In comfort air conditioning, where abstraction of both sensible and latent heat is required, the dehydration process must be supplemented by equipment for removing the total heat, both sensible and latent contributed by the process. This is shown on the psychometric chart by sensible cooling to a dry bulb temperature of 90°F, and partial rehumidification to a useful dry bulb temperature of 68°F.

The temperature increase and humidity decrease are functions of many factors including air flow rate, equipment design and type of desiccant employed. A survey of desiccants is found in the following section.

2.5.2.2 Desiccants

2.5.2.2.1 Calcium Chloride - Calcium chloride is one of the oldest used desiccants. The gas industry was one of the first industries to take advantage of its absorption properties in order to prevent corrosion in pipelines. Calcium chloride is also widely used to control the excess moisture found in basements during the summertime.

This chemical forms a number of hydrates. These are $CaCl_2 \cdot H_2O$, $CaCl_2 \cdot 2H_2O$, $CaCl_2 \cdot 4H_2O$, and $CaCl_2 \cdot 6H_2O$.

At temperatures below 86°F the overall reaction is

$$CaCl_2 + 6H_2O \longrightarrow CaCl_2 \cdot 6H_2O + 154,000 \text{ Btu}$$
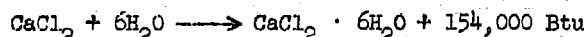
This equals 1430 Btu per pound of water of 143 Btu per man-hour. Since 1050 Btu are contributed from the latent heat of condensation, 380 Btu must come from the hydrate formation.

Calcium chloride is commonly used as a solid which dissolves into a solution of $CaCl_2 \cdot 6H_2O$ and water. At 80°F, the solid state is maintained through the formation of the hexahydrate. Any water absorbed after this dissolves the solid and a 2-phase system exists until the $CaCl_2$ holds 1.2 pounds of water for every pound of $CaCl_2$. After this the entire mixture exists as a solution.

The phase diagram in Figure 16 shows the phases and hydrates formed at various temperatures.

Because two phases are involved, a container is needed for the crystals and another one is needed to catch the drippings. The common household units consist of a wire mesh container which is placed in a pan or pail. As the solution forms, it runs down the bed and drops into the pan. The low cost of the material makes it feasible to discard the spent solution.
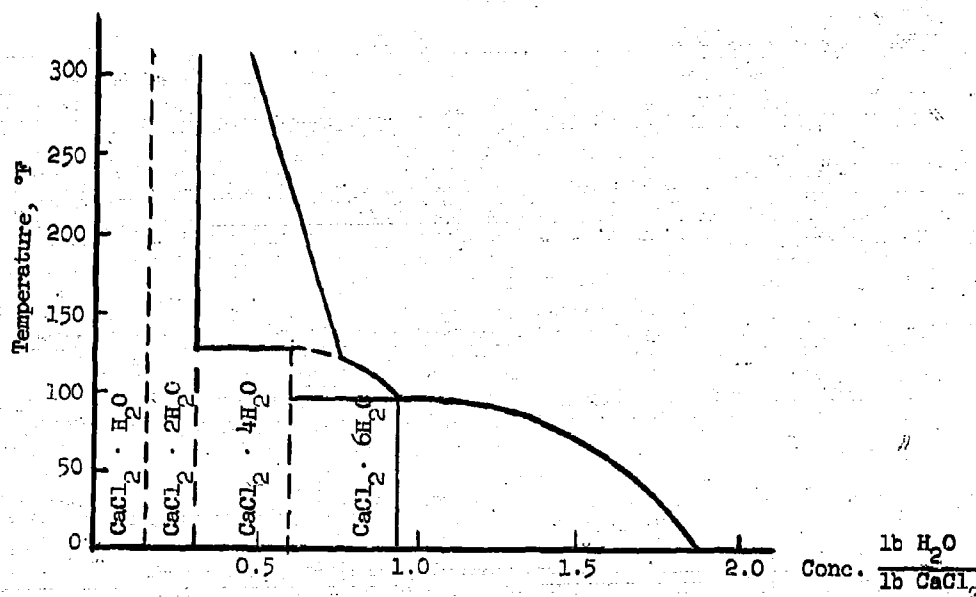
Figure 16   PHASE DIAGRAM FOR THE SYSTEM CALCIUM CHLORIDE-WATER (Ref. 71)

Hazards

Calcium chloride is nontoxic and as a pure material is noncorrosive; however, in solution it forms an electrolyte which promotes corrosion.

Capacity

The amount of calcium chloride required depends on the relative humidity which is to be maintained. Figure 17 shows the equilibrium capacity for various desiccants as a function of relative humidity.

The equilibrium moisture content at 50 per cent relative humidity is 1.8 pounds of water per pound of calcium chloride. This would mean that 0.555 pounds of desiccant are required per pound of water or 0.055 pounds per man-hour. Because these are equilibrium values, it is probably necessary to add extra desiccant. Using a factor of 150 per cent of the equilibrium requirements would bring the amount to 0.0832 pounds per man-hour or two pounds for 24 hours.
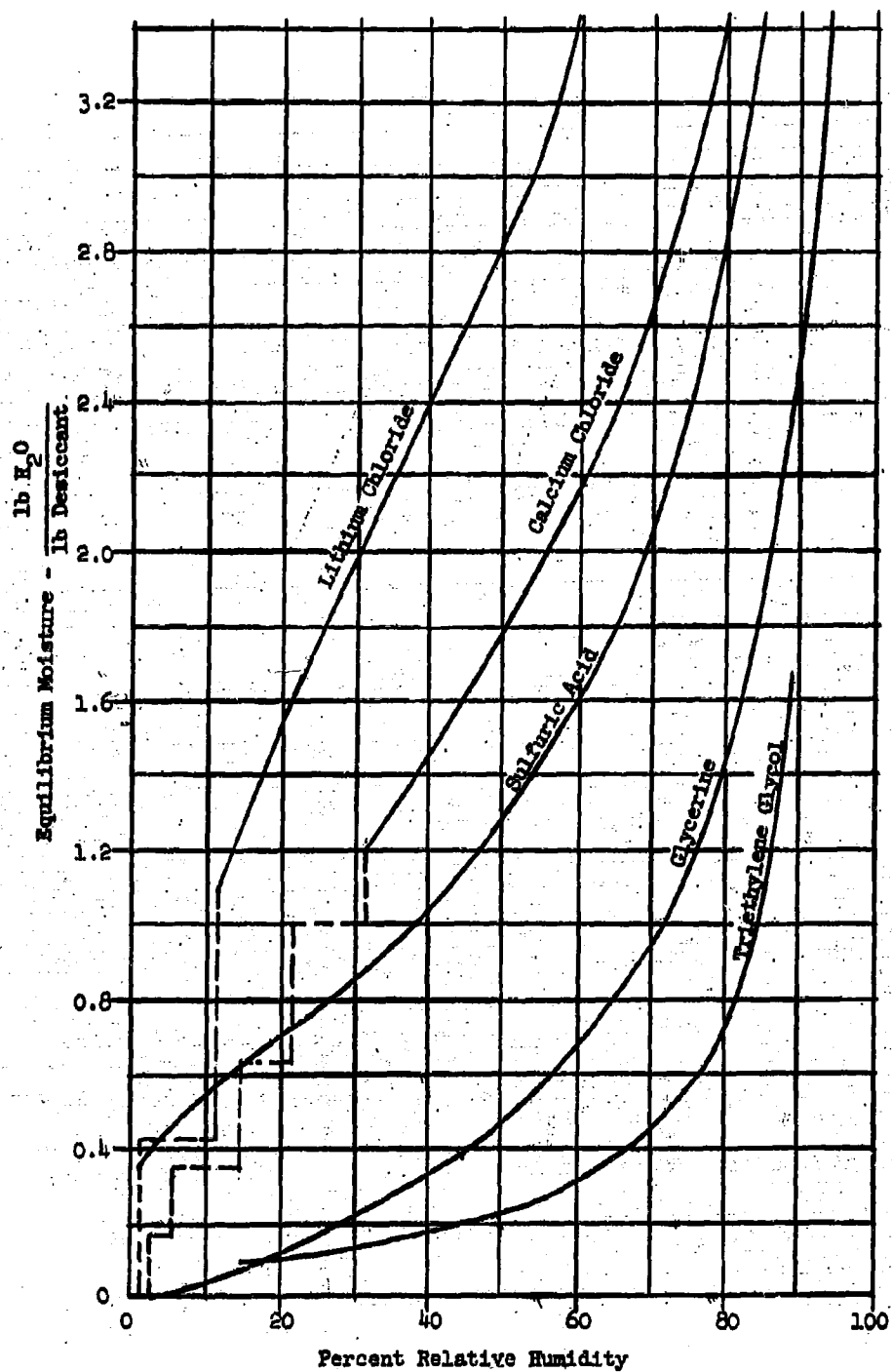
Figure 17 MOISTURE EQUILIBRIUM CURVES FOR VARIOUS DESICCANTS

Calcium chloride costs approximately $0.06 per pound for quantities under one ton and $0.02 for carload quantities. On the $0.06 per pound basis, the chemical cost per person for 24 hours would be $0.12.

The advantages of calcium chloride are high capacity and low cost. The disadvantage is the handling of the dripping of solution.

2.5.2.2.2 <u>Sodium Hydroxide or Potassium Hydroxide</u> - The hydroxides of sodium or potassium also react as dissolving solids to remove moisture from an environment. The reaction of sodium hydroxide is,

$$NaOH + H_2O_{(gas)} \longrightarrow NaOH \cdot H_2O + 24,300 \text{ Btu}$$
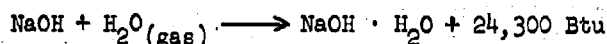
This is equivalent to 1350 Btu per pound of water or 135 Btu per man-hour.

The alkali hydroxides possess a strong dehydrating power as an anhydrous material. The surface soon becomes covered with a film of water and the rate is then dependent upon that of the saturated solution. The solution does not have as great a dehydrating power as the anhydrous form. (Ref. 72) The optimum working limits for alkali hydroxides are considered to be from 85 to 120°F for a saturated solution or a dissolving solid. (Ref. 73) Alkali hydroxides also absorb carbon dioxide and thus can be used for a dual purpose absorbent.

On the basis of the equation, $NaOH_{(anhyd)} + H_2O \longrightarrow NaOH \cdot H_2O$, 2.2 pounds of hydroxide are required per pound of water absorbed. The actual capacity at 70-80°F to maintain a relative humidity of 50 per cent would be greater than this. Assuming a capacity of 1 pound of hydroxide per pound of water removed, would require 2.5 pounds of desiccant per person for 24 hours. On the basis of a material cost of $0.08 per pound, the cost of stored material would be $0.20. For potassium hydroxide the material cost would be $0.11 per pound, so assuming the same capacity, the material cost would be $0.23 for 24 hours.

Alkali hydroxides have the disadvantage that they are toxic and corrosive. They react violently in the presence of strong acids.

Alkali hydroxides have no advantage over calcium chloride except that it will coabsorb carbon dioxide. The higher material cost, toxicity of material and corrosiveness tend to make calcium chloride a more suitable material.

2.5.2.2.3 <u>Lithium Chloride Solution</u> - Lithium chloride is a salt which may be used as a dissolving desiccant such as calcium chloride, however, when it is used, it is more commonly used in solution. At 80°F a concentrated solution contains 1.25 pounds of water per pound of chloride, while the equilibrium concentration at 50 per cent relative humidity contains 2.65 pounds of water per pound of chloride. Thus a concentrated solution could pick up 2.65 pounds of water.

The average amount of heat liberated during the absorption of 2.65 pounds of water with one pound of chloride equals 200 Btu (Ref. 74) per pound of LiCl or 110 Btu per pound of water. This is equivalent to 11 Btu per man-hour. If a saturated solution of lithium chloride is used, 65 Btu are liberated per pound of lithium chloride in absorbing from 2.65 to 1.25 pounds of water. Based on a pound of water, this equals 46.5 Btu or 4.65 Btu per man-hour. The values are for the salt and water. To them must be added the latent of condensation which is 1050 Btu per pound of water or 105 Btu per man-hour.

Hazards

Lithium chloride is nontoxic, but large doses taken internally may cause dizziness. It is also considered to be noncorrosive except toward alloys of magnesium. It is corrosive in the sense that it is a good electrolyte which will promote electrolytic corrosion.

If the lithium chloride is used as a saturated solution, 0.0715 pounds would be required per hour. In drum quantities, this would cost $0.86 per pound of salt or $0.0615 per man-hour. The stored material would be 1.72 pounds of solution per person for 24 hours or an investment of approximately $1.50. If the lithium chloride is used as a dissolving solid, 0.0378 pounds would be required per man-hour at a cost of $0.0325. On the basis of 24 hours, 0.9 pound would be required per person. This would cost $0.75.

Lithium chloride is a very good desiccant from the standpoint of capacity, low possible relative humidity, low heat of absorption. The only drawback is that it is several times as expensive as calcium chloride.

2.5.2.2.4 Sulfuric Acid - Sulfuric acid is effective in removing moisture from the air. At 50 per cent relative humidity, 1.25 pounds of water are absorbed by 1.00 pound or 100% acid.

The heat liberated when one pound of 100% acid absorbs 1.25 pounds of water is 275 Btu or 220 Btu per pound of water. Also 1050 Btu's must be added for the condensation of one pound of water. This amounts to 1270 Btu per pound of water vapor or 127 Btu per man-hour. Because 0.833 pounds of acid are required per pound of water, the amount of acid needed in a nonregenerative system would be 0.0833 pounds per man-hour or 2.0 pounds per person for 24 hours.

Hazards

Although sulfuric acid has a strong affinity for water, it would be un-advisable to use it for a shelter desiccant because it is very toxic and very corrosive. Also, since the primary carbon dioxide absorbents are strong bases, a violent reaction would occur if the acid came in contact with the carbon dioxide absorbent.

2.5.2.2.5 Phosphoric Acid (Phosphorus Pentoxide) - Phosphoric acid may be used as a desiccant. Its properties are similar to those of sulfuric acid; that is, it absorbs water with the liberation of heat but it is very toxic and corrosive.

The acid anhydride, phosphorus pentoxide, is a white crystalline solid which chemically combines with water to form phosphoric acid. The reaction is,

$$P_2O_5 + 3H_2O_{(g)} \longrightarrow 2H_3PO_4 + 112,000 \text{ Btu}$$
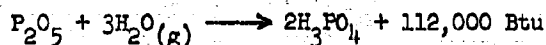
This is equivalent to 2070 Btu per pound of water or 207 Btu per man-hour. The anhydride is likewise corrosive and toxic.

2.5.2.2.6 Glycerine (Glycerol) - Glycerine is a hygroscopic liquid which will control the humidity in an environment.

The equilibrium capacity of glycerine at 50 per cent relative humidity is 0.45 pound of water per pound of glycerine. Thus 0.22 pound of glycerine is required per man-hour or 5.3 pounds per person for 24 hours. This would be slightly over 1 gallon of 100 per cent glycerine per person. Since the glycerine costs from $0.26 to $0.28 per pound, the investment would amount to approximately $1.50 per person for chemicals or $0.0625 per man-hour.

Glycerine is nontoxic and noncorrosive and is thus safe to handle. Glycerine has the advantages of safety and single-phase process and the disadvantage of being a liquid and having a cost several times as great as calcium chloride.

2.5.2.2.7 Glycols - Ethylene glycol, diethylene glycol, and triethylene glycol are hygroscopic liquids which absorb water from a moist atmosphere until an equilibrium is reached between the relative humidity and the concentration of the solution.

The capacity of glycol desiccants is lower than any of the liquid desiccants described thus far. As an example, the equilibrum capacity at 50 per cent relative humidity is approximately 0.25 pound of water per pound of desiccant. Thus 0.4 pound is required per man-hour and 10 pounds must be stored per person for 24 hours. The other glycols would have similar capacities.

On the assumption that 10 lbs of either of the three glycols is sufficient for a person for 24 hours, the costs would be $1.75 for ethylene glycol, $1.77 for diethylene glycol and $2.00 for triethylene glycol.

Hazards

The glycols are not extremely hazardous; however, they will cause disturbances if they are taken internally. Ethylene glycol is the worst offender in this matter. When compared to glycerine, the glycols are more toxic, costlier, and have less capacity.

2.5.2.2.8 Solid Desiccants - Under this title of solid desiccants are included nondissolving solids which adsorb by physical attraction such as silica gel or by chemical reaction such as calcium oxide.

2.5.2.2.9 Silica Gel - Silica gel is a widely used solid desiccant that has found use in many fields. The capacity of solid desiccants is less than that of dissolving solids or liquids but the solids have the greatest ease of handling and those which remove water by adsorption are easily regenerated. Silica gel is extensively used in packaging metal machinery parts in order to prevent corrosion.

The equilibrium capacity of silica gel at room temperature and 50 per cent relative humidity is 0.27 pound of water per pound of desiccant. At this capacity the heat of wetting equals 53 Btu per pound of desiccant. (Ref. 75) Thus the following quantity of heat is liberated during the adsorption of one pound of water.

Heat of Condensation $= 1050$ Btu

$$53 \text{ Btu/lb of desiccant} \times \frac{1 \text{ lb desiccant}}{0.27 \text{ lb } H_2O} = \underline{ 196 \text{ Btu}}$$

1246 Btu per lb of water.

Therefore for one person, 0.37 pound of desiccant is needed per hour and during this period 125 Btu's are liberated.

Costs

Silica gel costs from $0.25 to $0.30 per pound depending upon the quantity ordered. If 0.37 pound is required per man-hour, the cost per man-hour would be from $0.093 to $0.11.

2.5.2.2.10 Activated Alumina - Activated alumina is a solid desiccant which also removes water from an environment by physical adsorption. The capacity of activated alumina at 50 per cent relative humidity and 86°F is approximately 0.11 pound of water per pound of desiccant. The quantity of alumina would therefore be nearly one pound per man-hour.

If a regeneration system is used, provisions must be made to heat the spent desiccant and recool it to room temperature. If no regeneration is provided for, approximately 23 pounds must be stored per person for 24 hours.

The price of activated alumina is approximately $0.12 per pound so the cost per man-hour is approximately $0.12.

2.5.2.2.11 Molecular Sieves - Molecular Sieves are synthetic zeolites which after heating to remove water of crystallization become very porous and thus show a high attraction for water and other gaseous and liquid materials.

The equilibrium capacity is 0.22 pound of water per pound of Molecular Sieve for Type 4A sieve for relative humidities in the range of 50 per cent. For Type 13X sieve the capacity increases to 0.27 pound of water per pound of Molecular Sieve at 50 per cent relative humidity. For the Type 13X sieve, the requirement is 0.37 pound per man-hour and for the 4A type it is 0.455 pounds per man-hour.

In a nonregenerative system, the following quantities would be needed at the stated cost.

Type	13X	4A
Capacity lbs/man-hr	0.37	0.455
Pounds per person for 24 hours	8.9	10.9
Price $/pound	1.95	1.72
Adsorbent Investment	$34.70	$37.50

In a cyclic process in which the regeneration-adsorption is switched every hour, the cost of chemicals would be $1.44 for 13X sieve, and $1.56 per person for Type 4A. An extra investment would have to be made for regeneration equipment, so this method would still be costly.

Although Molecular Sieves are a very efficient moisture adsorbent, their high cost eliminates them from consideration for use in shelters.

2.5.2.2.12 Humi-Sorb (Culligan) - Humi-Sorb is a silica type desiccant manufactured by Culligan, Incorporated. Humi-Sorb is sold in units instead of by weight. The conversion factor is approximately 16 units per pound.

The capacity at 50 per cent relative humidity and 77°F is approximately 0.25 pounds of water per pound of Humi-Sorb. Therefore 0.4 pound or 6.4 units would be needed per man-hour. The requirement per person for 24 hours would be 9.6 pounds or 153 units. The 80-unit bags cost $1.29 to $1.06 depending upon quantity ordered. The maximum cost would be $2.50 per person or approximately $0.10 per man-hour. In quantity lots this can be reduced to $0.08 per man-hour.

Humi-Sorb has the advantage of being a solid packed in bags which are ready for service. It also leaves no drippings. Pricewise it is less expensive than silica gel but is much more expensive than calcium chloride.

2.5.2.2.13 Drierite - "Drierite" is a desiccant manufactured by the W. A. Hammond Drierite Company. Chemically it is anhydrous calcium sulfate which in the presence of a moist atmosphere forms the hemi-hydrate.

$$CaSO_4 + 1/2\ H_2O_{(g)} \longrightarrow CaSO_4 \cdot 1/2\ H_2O$$

The heat liberated during this reaction is 1590 (Ref. 76) Btu's per pound of water. According to this equation, 0.066 pounds of water react with one pound of drierite. The actual capacity is slightly higher than this because some additional water is taken up by physical adsorption. In "Du-Cal" industrial Drierite, the calcium sulfate is impregnated with calcium chloride in order to increase the capacity of the desiccant. The maximum working capacity of this material would probably be 0.1 pound of water per pound of desiccant, so one pound would be needed per man-hour. In 100-pound lots Du-Cal Drierite costs $0.22 per pound, thus the man-hour cost would be $0.22.

The cost of Drierite may be unattractive as a desiccant for fallout shelters when compared to other solid desiccants such as Humi-Sorb.

      2.5.2.2.14 <u>Anhydrone</u> - Anhydrous magnesium chlorate is known as "Anhydrone". In the presence of moisture, the anhydrous material passes through a di-, tri- and finally a hexahydrate.

$$Mg(ClO_4)_2\ 2H_2O \longrightarrow Mg(ClO_4)_2 \cdot 2H_2O \xrightarrow{H_2O} Mg(ClO_4)_2 \cdot 3H_2O$$

$$\xrightarrow{3H_2O} Mg(ClO_4)_2 \cdot 6H_2O$$
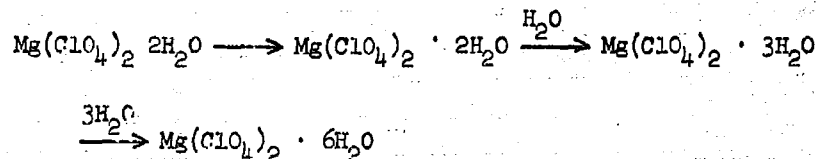
The anhydrous material absorbs 48.6 per cent of its original weight in forming the hexahydrate. Thus to absorb 0.1 pound of water per man-hour would require 0.206 pound of anhydrone in an ideal system. This is attractive from a weight and volume viewpoint; however, the high cost make the use of Anhydrone prohibitive. The cost per pound is approximately $2.00. This would make the per man-hour cost $0.40.

The material can also form explosive mixtures if it comes in contact with organic vapor, so even if it were less expensive, it would have to be rejected for this reason.

      2.5.2.2.15 <u>Calcium Oxide</u> - Lime is hygroscopic and absorbs water to form the hydroxide. Theoretically one pound of lime should absorb 0.32 pound of water, but the actual capacity is 0.1 pound of water per pound of lime or less because of the formation of carbonates. On the assumption that the capacity is 10 per cent of the dry weight, one pound of lime would be required per man-hour.

      2.5.2.2.16 <u>Barium Oxide</u> - Barium oxide reacts with water to form the hydroxide and the hydroxide then forms a monohydrate and a octohydrate.

The hydroxide is extremely stable. In fact, barium hydroxide can be used for moisture removal at temperatures as high as 1000°F. The primary drawback is low capacity. Barium hydroxide absorbs only 10 per cent of its dry weight in water. Therefore one pound is necessary per man-hour. Since the cost of ground material in drum lots is approximately $0.15 per pound, the cost per man-hour would be $0.15.

The material is also toxic and is hazardous in this respect.

2.5.2.2.17 Activated Carbon - Activated carbon is used exten-
sively as an adsorbent. It is capable of adsorbing water, odors, organic
compounds and various other substances. While substances such as Molecular
Sieves and silica gel adsorb water in preference to carbon dioxide or organic
vapors, activated carbon acts in the reverse manner. That is, any water which
is adsorbed can be replaced by organic vapors. (Ref. 77)

Since there would certainly be organic vapors present from human sweat or
flatus, and cooking, the activated carbon would not be as efficient as a
desiccant as one which adsorbed water in preference to other vapors.

2.5.2.3 Comparison of Various Desiccants

Type	Reli-ability	Power Requirement	Cost per Man-hour	Storage & Handling
Deliquescent Solids				
Calcium Chloride	Good	None	Very low	Fair
KOH, NaOH	Good	None	Low	Fair
LiCl Solid	Good	None	Low	Fair
Phosphorus Pentoxide	Good	None	Low	Poor
Solutions				
LiCl	Good	None	Moderately Low	Good
Sulfuric Acid	Good	None	Low	Poor
Phosphoric Acid	Good	None	Low	Poor
Glycerine	Good	None	Moderately Low	Good
Glycols	Good	None	Moderately Low	Good
Solids				
Silica Gel	Good	None	Moderate	Good
Activated Alumina	Good	None	Moderate	Good
Molecular Sieve	Good	None	Very High	Good
Humi-Sorb	Good	None	Moderate	Good
Drierite	Good	None	High	Good
Anhydrone	Good	None	High	Fair
Calcium Oxide	Fair	None	Low	Good
Barium Oxide	Fair	None	Moderate	Fair
Activated Carbon	Fair	None	High	Good

Moisture control is not essential for life support, but it is necessary from the standpoint of morale, comfort, and prevention of colds. Reference is made to Figure 3 for this comparison.

Reliability

Deliquescent Solids - Deliquescent materials are reliable desiccants, however, alkali hydroxides form a surface film which decreases the rate of water absorption.

Solutions - Solutions of desiccants are reliable although they do not have the capacity of a deliquescent material.

Solids - The solid desiccants, silica gel, activated alumina, Molecular Sieves, Humi-Sorb, Drierite, and Anhydrone adsorb moisture efficiently. Oxides of calcium or barium will form carbonate which will hinder further adsorption. Activated carbon will preferentially adsorb high molecular weight compounds.

Power Requirements

None of the desiccants require power for operation although a blower would increase the rate of adsorption. Power is required if regeneration is required.

Costs

The costs of desiccants listed below are based on chemical prices and a nonregenerative system. Regeneration will lower chemical costs but raise equipment costs and also necessitate a power supply.

TABLE 15

COSTS OF DESICCANTS

Compound	Dollars per Man-Hour
Calcium Chloride	0.002-0.004
NaOH - KOH	0.008-0.011
LiCl (solid)	0.032
P_2O_5	0.045
LiCl (sat. soln.)	0.069
Sulfuric Acid	0.001
Phosphoric Acid	Low
Glycerine	0.063
Glycols	0.088
Silica Gel	0.10
Activated Alumina	0.12
Molecular Sieves	0.886
Humi-Sorb	0.10
Drierite	0.22
Anhydrone	0.40
Calcium Oxide	0.01
Barium Oxide	0.15
Activated Carbon	Moderate

Storage and Handling

Deliquescent desiccants must be stored sealed. Other than this, there is no storage problem. The main problem of handling the chlorides of calcium or lithium come from the fact that the deliquescent materials drip a saturated solution and require a pan to catch this solution. This solution is nontoxic but may be corrosive. The hydroxides of sodium or potassium on the other hand are not only corrosive but are also toxic. They do have secondary effect of also scrubbing carbon dioxide. Phosphorus pentoxide is also corrosive and toxic.

Solutions - Solutions of lithium chloride, glycerine and glycols are easy and safe to handle. Sulfuric and phosphoric acid solutions are toxic and corrosive.

Solids - The solid desiccants are easily handled, and for the most part are safe to use. The exception is Anhydrone, which is a perchlorate and is capable of forming unstable mixtures in the presence of combustible substances. Barium oxide is rated fair instead of good because it is a toxic compound.

Of the desiccants investigated, the following will be further considered because of the following features:

        Calcium chloride - very low cost, high capacity

        Silica gel   - moderate cost, handling ease

        Humi-Sorb   - Moderate cost, handling ease

2.5.3 Heat Rejection Methods

To provide temperature control in an underground shelter sensible heat must be transferred from the shelter to a suitable external heat sink, such as the surrounding soil or proximate well water. Temperature control methods include both active (mechanical refrigeration) and passive techniques.

2.5.3.1 Mechanical Refrigeration Systems

2.5.3.1.1 Vapor Compression System - The most common refrigeration method used in air conditioning applications today is the vapor-compression system, so-called because the refrigerant is in vapor form when raised from the low temperature to the high temperature by compression. The most common refrigerants used, especially in air conditioning application, are the Freons such as Freon 12 (dichlorodifluoromethane). Freon has two distinctive and important advantages for shelter refrigeration systems, namely, it is nontoxic and nonflammable. A schematic of a basic vapor compression system is shown below.
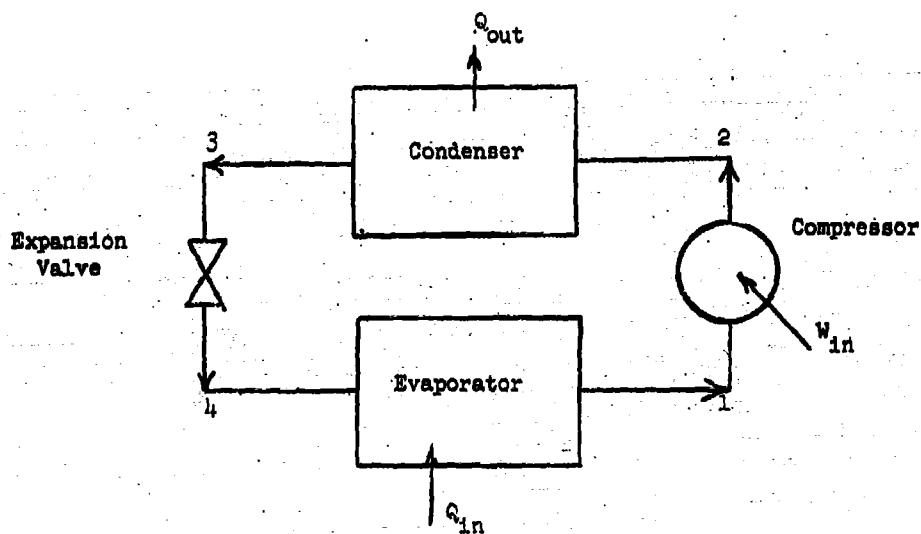
Figure 18 FLOW DIAGRAM FOR VAPOR COMPRESSION SYSTEM

An explanation of the thermodynamics taking place is best made by reference to a temperature-entropy diagram as shown below:
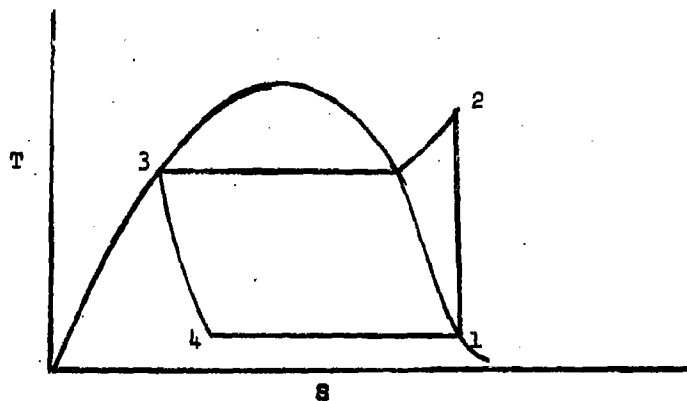
Figure 19 TEMPERATURE-ENTROPY DIAGRAM FOR VAPOR COMPRESSION SYSTEM

Beginning at point 1, the refrigerant vapor enters the compressor, which may be either a reciprocating or centrifugal type. The low temperature refrigerant is compressed (isentropically in the ideal case) to some pressure, p_o, such that the corresponding saturation temperature is above that of the temperature to which heat is to be rejected in the condenser, which may be either air-cooled or water-cooled. The condenser removes any superheat, the latent heat of condensation, and generally subcools the liquid a small amount. From 3 to 4 the refrigerant is throttled through the expansion valve at constant enthalpy. The saturated liquid at state 3 thus becomes a very wet mixture of liquid and vapor at 4. From 4 to 1 the mixture absorbs its latent heat of vaporization from the area which is to be cooled.

The coefficient of performance, which is a ratio of the heat absorbed in the evaporator to the heat equivalent of work done by the compressor, may be expressed as,

$$c.o.p. = \frac{h_3 - h_1}{h_4 - h_3}$$

where, h = enthalpies at the state point indicated by subscripts, Btu/lb.

For a Freon 12 system operating with a condensing temperature of 120°F and an evaporator temperature of 40°F, assuming isentropic compression and constant enthalpy expansion, the coefficient of performance is,

$$c.o.p. = \frac{82.7 - 36.2}{93.5 - 82.7} = \frac{46.5}{10.8} = 4.3 .$$

The theoretical horsepower per ton of refrigeration (12,000 Btu/hr) and the coefficient of performance are inverse functions as shown by,

$$HP/ton = \frac{4.717}{c.o.p.}$$

For the example given,

$$HP/ton = \frac{4.717}{4.3} = 1.1 .$$

Each pound of Freon 12 absorbs 46.5 Btu of heat passing through the evaporator.

2.5.3.1.2 <u>Air Refrigerating Cycle</u> - Air itself is used as a refrigerant in this system, which does not entail a change-of-phase and the consequent latent heats of vaporization and condensation as did the previous system described. The equipment schematic for this system is presented next.
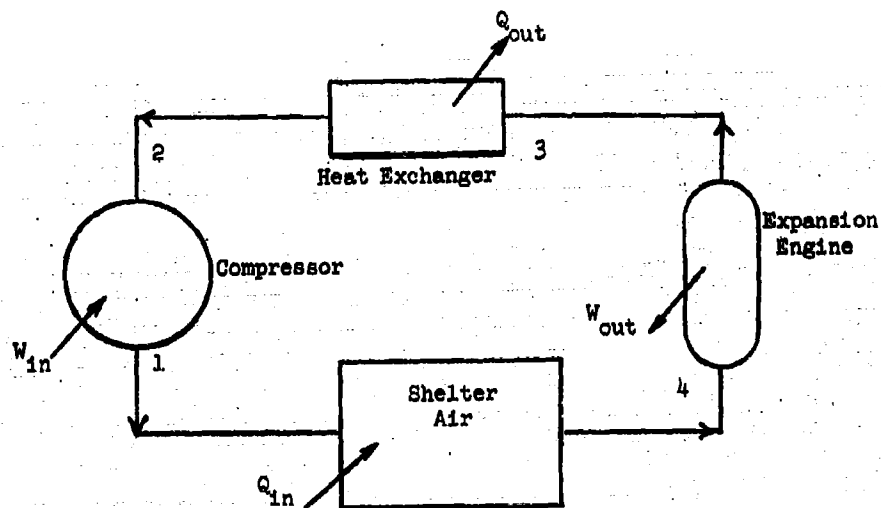
Figure 20   FLOW DIAGRAM FOR AIR CYCLE SYSTEM

The ideal process is shown thermodynamically on the temperature-entropy diagram below:
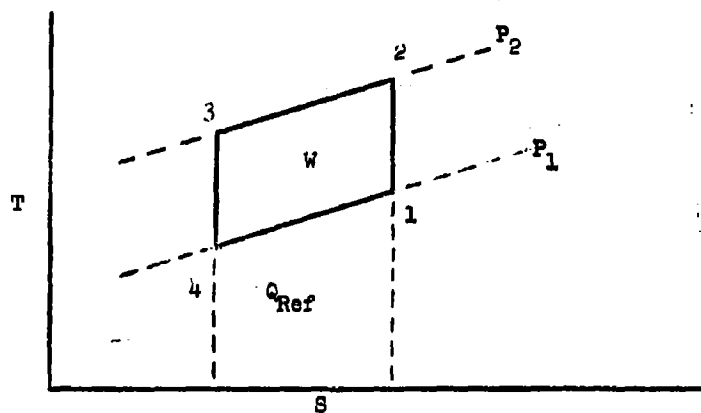
Figure 21   TEMPERATURE-ENTROPY DIAGRAM FOR AIR CYCLE SYSTEM

As shown, air at P_1 is drawn directly from the shelter into the compressor when isentropic compression to P_2 occurs. From 2 to 3 constant pressure cooling of the air takes place by heat rejection to water or some other acceptable heat sink. From 3 to 4 the air is isentropically expanded through an expansion engine, such as a turbine, directly into the shelter at temperature, T_4, which is lower than the intake temperature, T_1.

The area, a-3-2-b, represents the heat rejected in the heat exchanger, while the area a-4-1-b represents the cooling effect.

The coefficient of performance is the cooling effect, area a-4-1-b, divided by the net work, area 1-2-3-4. Assuming isentropic compression and expansion the coefficient of performance may be expressed by,

$$c.o.p. = \frac{T_1 - T_4}{(T_2 - T_1) - (T_3 - T_4)}$$

To compare the theoretical coefficient of performance of the air cycle to that of the vapor compression cycle for Freon 12, it will be assumed that the temperature entering the compressor, T_1, is equal to the evaporating temperature and the temperature leaving the cooler, T_3, is equal to the condenser temperature. Figure 22 shows the effect of pressure ratio upon coefficient of performance and heat absorbed per pound of fluid circulated. As shown, a theoretical coefficient of performance of 3.5 is obtained with a pressure ratio of 2.5, but only 12.5 Btu of heat are removed per pound of air pumped. Higher pressure ratios yield greater refrigeration effects per pound of air but at the expense of decreasing coefficients of performance. A point of diminishing returns must be established in the actual case where the frictional losses due to pumping larger volumes of air offset the greater coefficients of performance.

The Freon 12 vapor compression system with a refrigeration effect of 46.5 Btu per pound of refrigerant and a coefficient of performance of 4.3 is superior to any air cycle system operating between the same temperature limits. Air cycle equipment would also be larger because of the larger amounts of gas which must be handled.

In general, an air refrigeration system is superior to a vapor compression system in freedom from refrigerant leakage but requires more power for the same refrigeration effect.

For shelter applications, however, the reliable and completely safe operating characteristics of the air cycle system may outweigh the requirement for more power. Consider an air refrigeration system operating with an inlet temperature of 80°F and a temperature drop through the cooling coils of 50°F. Table 17 shows the theoretical coefficients of performance and refrigeration effects for various pressure ratios. A trade-off study could be made to select the optimum pressure ratio for minimum power consumption.
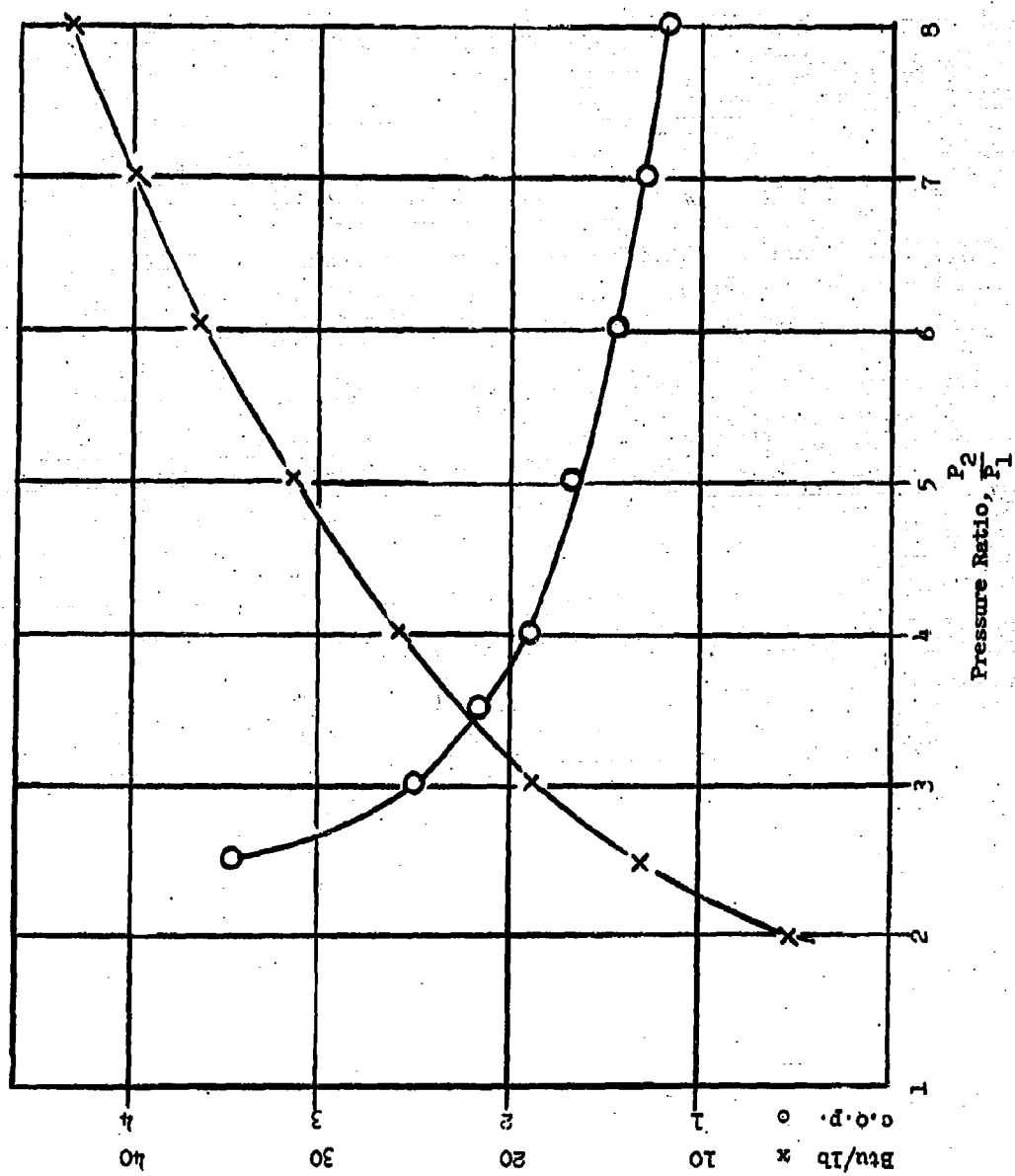
Figure 22 AIR CYCLE REFRIGERATION PERFORMANCE

$T_2 = 40°F$, $T_3 = 120°F$

Pressure Ratio, $\frac{P_2}{P_1}$

c.o.p., o

Btu/lb x

96

TABLE 16

THEORETICAL PERFORMANCE OF AIR CYCLE SYSTEM
(Inlet Temp = 80°F, Cooler $\Delta T = 50°F$)

Pressure Ratio	Comp. Inlet Temp.°F	Comp. Outlet Temp. °F	Cooler Outlet Temp. °F	Expander Outlet Temp. °F	Coefficient of Performance	Refrigeration Effect Btu/lb
1.5	80	148	98	35	7.94	10.6
2.0	80	198	148	40	4.57	9.85
2.5	80	242	192	42	3.33	9.2
3.0	80	279	229	43	2.87	8.9
3.5	80	312	262	45	2.33	8.4
4.0	80	342	292	46	2.06	8.1
5.0	80	396	346	48	1.71	7.5
6.0	80	442	392	50	1.49	7.2
7.0	80	482	432	51	1.34	6.9
8.0	80	517	467	52	1.23	6.6

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2.5.3.1.3 Absorption System - Absorption refrigeration systems are heat-operated and utilize at least two working substances, a refrigerant and an absorbent for the refrigerant. A simple continuous cycle for a liquid absorbent is shown in Figure 23.
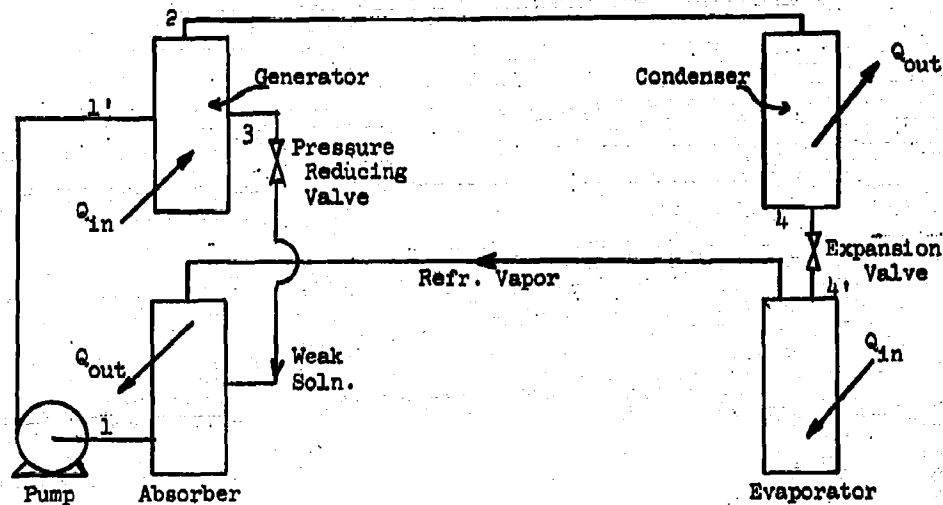
Figure 23 FLOW DIAGRAM IN ABSORPTION REFRIGERATION SYSTEM

The four major steps of this cycle are latent-heat processes involving the transfer of refrigerant between the liquid and vapor states in the evaporator, absorber, generator, and condenser. In the evaporator, nearly pure liquid refrigerant boils and absorbs the cooling load. In the absorber, the vapor from the evaporator is absorbed by a weak solution producing a stronger solution and waste heat which must be rejected to a heat sink. The rich solution is then pumped to the generator where a high temperature source of heat is used to boil out refrigerant vapor. The vapor then passes to the condenser, where it condenses and evolves waste heat to be rejected to a heat sink, such as cooling water. The generator and condenser operate at the high side pressure. The weak solution produced in the generator is fed to the absorber through a valve, and the liquid refrigerant produced in the condenser is fed to the evaporator through another valve.

A factor expressing the efficiency of absorption refrigeration systems, which is comparable to coefficient of performance is called the performance factor. Performance factor is the ratio of the heat absorbed in the evaporator to the heat absorbed in the generator, and is equal to slightly less than one for the ideal case under all circumstances. The performance factor decreases slightly as the difference between evaporator and absorber temperature is increased. In comparing the absorption system with a vapor compression system it is noted that the performance factor has an upper limit of one.

In comparing the absorption system to the vapor-compression system the value of the particular type of energy required must be considered rather than the amount. The cost of the absorption machine, both initial and operating, is less influenced by the evaporating temperature than that of the vapor-compression machine, so that at low temperatures the absorption machine compares favorably. The absorption machine has certain particular advantages for shelter applications: (1) no prime moving parts, (2) no lubrication is required, (3) easy to control at partial load while maintaining its full load efficiency, (4) heat is often easier to supply than electrical power.

For shelter applications, however, very low evaporator temperatures are not required. If heat and power are considered equally difficult to supply then the absorption system is inferior to both the vapor compression and air cycle systems as indicated by the performance factor.

2.5.3.2 Passive Cooling Techniques

Passive cooling techniques are those requiring little or no external power to transfer heat from the shelter to either an external or internal sink.

2.5.3.2.1 Circulation of Well Water - An obvious method of rejecting heat is by circulating well water from outside the shelter through an internal heat exchanger. Since it is very likely that many shelters will be built to include a well water supply, this method is convenient, but does require power for a water pump and circulation fan. The power required to provide a certain cooling effect, Q, is directly proportional to the quantity of water pumped. The quantity of water pumped, m, is inversely proportional to the temperature change, Δt, across the heat exchanger as shown by,

$$m = \frac{Q}{\Delta t} \; .$$

Therefore, the required power consumption rate is largely dependent upon the temperature of well water in the particular shelter location. In addition to a pump and heat exchanger, a circulation fan to force shelter air across the heat exchanger is required.

A serious disadvantage of this system is that the well water temperature also dictates the minimum dew point which can be obtained in the environment.

2.5.3.2.2 <u>Latent Heats of Fusion</u> - The latent heat of fusion of solids such as ice may also be considered for a means of absorbing the sensible heat of a shelter. Ice absorbs 144 Btu/lb upon melting and if a temperature increase of 30°F is assumed then each pound of ice is capable of absorbing about 174 Btu. If metabolic heat is assumed to be 400 Btu/hr per man it is readily seen that about 2.3 pounds of ice are required for each man per hour of occupancy for metabolic heat removal alone, which is a prohibitive amount. No other common materials having higher latent heats of fusion possess low enough melting temperatures for such application.

2.5.3.2.3 <u>Latent Heats of Vaporization</u> - Vaporization of a liquid is an effective way of absorbing sensible heat. Water, with a latent heat of 1060 Btu/lb (at 60°F), absorbs more energy upon vaporization than does any other common liquid. Vaporization at 14.7 psia does not take place until temperatures of 212°F are attained, however. To vaporize water at 60°F, for example, the pressure must be reduced to 0.256 psia necessitating incorporation of a high capacity vacuum pump and an evaporator-heat exchanger.

Ammonia has a high latent heat of vaporization (518 Btu/lb at 60°F) but introduces problems of corrosion and toxicity into a shelter system. Of the readily available liquids that can be handled easily, propane has the highest latent heat of vaporization (184 Btu/lb at 60°F). The heat of vaporization for propane is thus seen to be only slightly greater than the heat of fusion for ice.

Since propane is a fuel it could also be used for auxiliary power generation and the electrical power used to drive a mechanical refrigeration system. The cooling capacity, Q, of such a system can be calculated as follows:

$$Q = m \ (h_{pg} + H \eta_g \ COP)$$

where

Q = cooling capacity, Btu/hr

m = flowrate of fuel, lb/hr

h_{fg} = latent heat of vaporization of fuel, Btu/lb

H = heating value of fuel, Btu/lb

η_g = generator system efficiency

COP = coefficient of performance of refrigeration unit, assume a value of 6.

To produce a cooling effect equal to the metabolic heat production of one man, about 0.2 lb/hr of propane are required. Thus, this system could effectively be used to provide sensible cooling but the effect of vaporization is small compared to the combustion energy.

2.5.3.2.4 **Heat of Solution** - Many materials release or absorb thermal energy when dissolved in water. The following three salts absorb thermal energy upon dissolving in water. These are examples of a number of compounds listed in Perry's Handbook having a negative heat of solution.

Compound (C)	Heat Absorbed @ 64°F	Amount of Water for Dilution
Sodium diphosphate $Na_2HPO_4 \cdot 12H_2O$	117 Btu/lb_c	80.3 lbs/lb_c
Sodium Thiosulphate $Na_2S_2O_3 \cdot 5H_2O$	81.8	29.0
Sodium tetraborate $Na_2B_4O_7 \cdot 10H_2O$	79.4	42.5

It is seen that prohibitive quantities of chemicals would be required to absorb the heat loads anticipated in underground shelters. Also large quantities of water would be required to form the solution.

2.5.3.2.5 **Thermal Buss Bars** - Since the soils surrounding underground shelters are relatively poor thermal conductors, little thermal energy is transferred through conventional shelter walls. (See Table 14) If the heat transfer through the soil is considered one-dimensional and the soil is regarded as an infinitely thick heat sink, then the total heat flow during an interval of time is,

$$Q = 1.13 \ k \ \theta_i \frac{t}{\alpha}$$

where, Q =   total heat flow during interval, Btu/ft^2

   k =   thermal conductivity of soil, Btu ft/hr - ft^2-°F

   θ_i =   temperature differential between soil and air, °F

   t =   interval of time concerned, hr.

   α =   diffusivity of soil, $\frac{k}{C_m \rho}$, ft^2/hr

A system requiring no power to improve heat transfer utilizes several fixed conductance heat paths to improve the overall conductivity through the soil. These fixed conductance paths are termed thermal buss bars and are fabricated of some reasonably inexpensive and relatively high conductivity metal. Shown next is a cost and conductivity comparison for aluminum, copper, and steel buss bars.

Material	Conductivity	Cost
Copper	226 Btu-ft/hr-ft^2-°F	$0.10/in^3
Aluminum	117	.03
Steel	36	.01

The comparison clearly shows that aluminum provides the highest conductivity per dollar.

Since the buss bars must project about 4 ft. into the soil the conductivity of the aluminum bars is 29 Btu/ft^2-hr-°F. The above equation may be used to calculate the required conductivity of the soil-buss for combination, k_R. The ratio of aluminum per unit area of soil, x may then be calculated as below.

$$x = \frac{k_R - k_S}{29 - k_S}$$

where, x = ratio of aluminum area to soil area

  k_R = required conductivity of combustion, Btu/hr-ft^2-°F

  k_S = soil conductivity, Btu/hr-ft^2-°F.

To incorporate such a thermal control system would require: (1) a series of convective heat exchangers located inside the shelter, (2) a number of thermal buss bars projecting into the soil, (3) a thermal control switch to provide some means of controlling the amount of heat rejected, which might be required in cool climates to prevent overcooling of the shelter interior.

Control of this system could be provided by means of a switch which connects and disconnects the convective heat transfer panels from the shelter end of the thermal buss bars. The thermal switch itself is any device which will break the circuit. Simple bimetallic devices can be used, but the thermal contact resistance of these devices is usually high. A superior system utilizes a bellows filled with a temperature-sensitive fluid to actuate the switch contacts. The fluid may operate on the volume variation produced by a phase change or simply by expansion and contraction to temperature change.

For shelters located in relatively cool climates, the thermal buss bar method is most attractive. Many shelters may thus be afforded temperature control without expending power.

SECTION 3

EXPERIMENTAL EVALUATIONS

Section 2 of this report demonstrated the superiority of soda-lime and Baralyme over other types of carbon dioxide absorbents when used in a dynamic system. However, the literature and field survey also conducted under Section 2 failed to uncover sufficient experimentally determined performance data upon which application specifications could be based. Therefore, experimental evaluations were undertaken to obtain optimization data for absorbent canister design.

As mentioned in Section 2, the use of lithium hydroxide anhydrous crystals for static absorption of carbon dioxide in small family fallout shelters has been nationally advertised. Experimental results upon which application designs could be based were found lacking, therefore, static absorption tests of this absorbent were conducted in a sealed 500 cubic-foot chamber.

Since chlorate candles have been advertised as a source of oxygen in fallout shelters, a 90 cubic-foot candle was obtained and tested to establish the ease of operation, safety, and performance of these items.

3.1 Dynamic Absorption Systems

3.1.1 Test Objectives

The removal of CO_2 by solid absorbents with forced ventilation is a problem of gas absorption in packed beds. Estimation of the concentration of a fluid stream and the capacity of the absorbent bed present formidable mathematical difficulties which have not been completely solved for the general case.

Marshall and Hougen (Ref. 78) have developed a solution for the special case where adsorption (the two terms "adsorption" and "absorption" have clearly defined differences but are used interchangeably to include both meanings) takes place from a dilute solution and where equilibrium adsorption is directly proportional to the concentration. Danby and coworkers (Ref. 79) presented "The Kinetics of Absorption of Gases from an Air Stream by Granular Reagents" in which the assumptions were irreversible chemical reaction between the absorbent and the gas or at least irreversible adsorption. The latter approach was used here because of the minimum amount of experiment necessary to obtain design data.

The materials examined in the present investigation were packed columns of soda-lime and Baralyme. Existing information on the performance of these chemicals was inadequate to enable an optimum process design. Therefore, a series of experiments were carried out to obtain kinetic data in the form of breakthrough time and capacity as functions of vessel dimensions and flow rate.

3.1.2 Theory

For the theoretical equation, consider a column of unit cross section. A distance ℓ from the bottom there is a zone with thickness $d\ell$ and the concentration of the absorbate in the stream entering the zone is $C_{\ell,T}$ and leaving the concentration is $C_{\ell,T} + (\partial C/\partial \ell)_T \, d\ell$, where T is the total time the column has been exposed to the stream. If x is the amount of gas reacted per unit volume of material, then the amount reacted during dT in the zone is

$$A \cdot d\ell \; \left(\frac{\partial x}{\partial T}\right)_\ell \; dT \tag{1}$$

where A is the cross-sectional area of the column. The standard equation of continuity for a binary mixture applied in this situation:

$$-\frac{\partial C}{\partial \ell} = \frac{1}{V}\left(\frac{\partial x}{\partial T} + \frac{\partial C}{\partial T}\right) \tag{2}$$

where V is the superficial velocity (volume flow divided by the cross-sectional area). In essence the equation states that the difference between the concentration of the absorbate-in minus the absorbate-out is equal to the absorbate reacted in the zone plus the rate of change of its concentration with time in the zone. To obtain a reasonably simple mathematical treatment, the following assumption must be made concerning the kinetics of the reaction. The rate of removal of the gas (carbon dioxide in this case) is directly proportional both to the concentration in the stream and the concentration of active centers remaining in the material at any given time. Thus a relation between x and C is given:

$$\frac{\partial x}{\partial T} = kCN \tag{3}$$

where k is a constant and N is the number of active sites per volume of material. Since each active center as defined above is consumed with one molecule, then it follows,

$$-\frac{\partial N}{\partial T} = \frac{\partial x}{\partial T} = kCN \tag{4}$$

These simultaneous equations combined with Eq. (2) are solved to obtain C as a function of both ℓ and T. The general solution combined with the boundary condition at $\ell = 0$, $C = C_o$ (C_o is the entering gas) and a limiting condition $C = C_o \, e^{-kN_o \ell/V}$ at $T = 0$ given the final relation,

$$C = \frac{C_o}{e^{-kC_o T} \left(e^{kN_o \ell/V} - 1\right) + 1} \tag{5}$$

where N_o is the initial number of active sites. Other assumptions implied in the solution are that the heat of reaction or adsorption is conducted away immediately, and changes in local water content in the column do not appreciably change the rate of removal of the gas.

Equation (5) is very flexible since all the significant variables; namely, column length, time, and outlet concentration are contained in it. Upon rearranging Eq. (5), the following is obtained,

$$\ln \ (C_0/C - 1) = - kC_0 T + \ \ln(e^{kN_0 \ell/V} - 1) \tag{6}$$

For a given set of conditions such as the velocity, the length, and the inlet concentration, a linear relation exists between $\ln(C_0/C - 1)$ and T. The constants k and N_0 can be determined from a plot of this data in the early stages of breakthrough when C_0/C is finite. It is possible that the process is diffusion-controlled; that is, the diffusion of CO_2 to the particle surface from the bulk stream is much slower than the reaction.[2] In this event, k and N_0 will be dependent on the velocity, and should follow a relation such as k proportional to the square root of the velocity.

The concentration of the outlet stream at which the column is no longer considered useful is known as the "breakthrough concentration". Corresponding to this is the time at which this occurs, the "breakthrough time". Because it is usually true that $e^{kN_0 \ell/V}$ is much greater than unity, the breakthrough time is approximately linear with column length, and inversely proportional to the velocity. This is seen from inserting the last assumption in Eq. (6):

$$\ln \ (\frac{C_0}{C'} - 1) = - kC_0 T' + \frac{kN_0 \ell}{V} \tag{7}$$

where C' is the breakthrough concentration, and T' is the corresponding time.

The experiments were planned from consideration of the theoretical performance predicted by Eq. (7). With given conditions of packing height, inlet concentration, outlet breakthrough concentration, the superficial velocity was varied for each run. It could be expected from the theory that plots of T' vs $1/V$ would be straight lines, one for each length. A knowledge of T' enables the calculation of the capacity of the bed in pounds of CO_2 per pound of bed from the known weight of bed, the flow rate, and the inlet concentration. Similar plots could then be constructed as capacity versus $1/V$ for each length of the corresponding cross-plot, length versus capacity for each velocity. Extrapolation of such charts during the process of experimentation enabled the intelligent selection of test variables for subsequent runs.

3.1.3 Test Procedure

Experimental procedures involved in testing the two absorbents were aimed at simulating typical shelter conditions. The average laboratory temperature during these tests was 80°F and the relative humidity was 70 to 80 per cent. A Roots-type, rotary-lobe blower was used to circulate room air through the system. Carbon dioxide was injected in the air stream at a rate necessary to produce a one-per cent mixture in the inlet to the absorbent bed. The one-per cent

concentration was used in order to fulfill the physiological requirement that the shelter air be controlled at one-per cent carbon dioxide or below.

A flow diagram of the apparatus is shown in Figure 24. A cylinder of compressed carbon dioxide was used as the carbon dioxide source for inlet stream. In order to maintain a constant pressure and flow of carbon dioxide the pressure in the cylinder was adjusted through two reduction valves to 2.5 psi. Fine control of the carbon dioxide flow was accomplished with a small needle valve. A column by-pass enabled the inlet flow to be monitored by the sensor prior to an actual experimental run. In this manner, it was possible to adjust the carbon dioxide to one per cent and also check the concentration at any time during the run. The total stream flow rate was set by adjusting the blower by-pass and outlet valves.

The effluent gas from the column was partially vented to the atmosphere. The remainder was circulated to the carbon dioxide sensor with a constant-volume diaphragm pump. Another vent was provided prior to the sensor inlet to remove water condensed in the Tygon tubing. A recorder was used in conjunction with the sensor to give a continuous record of the effluent concentration.

The first series of tests were conducted in a six-inch diameter (5.44-in. I.D.) Plexiglass column. Only one bed length of 13 inches was tested in this column. The remainder of tests were run in a 1.5-inch I.D. glass tube with the bed length varying from 13 to 39 inches. Comparable conditions in the two columns gave results which agreed within experimental error; therefore, the smaller column was used in order to conserve material and to decrease the time required for each test. Several flow rates were run at each of three packing lengths, namely 13, 20 and 26 inches. One test with a 39-inch bed length was necessary to verify scale-up designs. Superficial velocities varying from 0.28 to 1.0 foot per second were tested at each of the latter three bed lengths.

The particle sizes of both soda-lime and Baralyme were the low dust 4-8 mesh types. Fresh absorbent was closely packed in the column for each run by tapping the outside vigorously when each third of the total length was filled. During the majority of a typical run, the effluent carbon dioxide concentration was approximately zero. The period during which the outlet changed from zero to 0.1 per cent was small compared to the total time, and thus all but a negligible amount of carbon dioxide was absorbed.

3.1.4 Test Results

The data collected for each run consisted of the total gas flow rate, breakthrough time, bed temperature, packing length, and packing weight. Pressure drops were determined in a separate experiment. All the other important variables can be calculated from these measurements. The total weight of CO_2 absorbed is determined from the breakthrough time, the temperature and one per cent of the total flow rate. Velocity is calculated directly from the bed diameter and the flow rate, therefore it is considered superficial; that is, the velocity which would result at the given volume flow rate if the column was empty. The data and pertinent calculated variables are listed in Table 17.
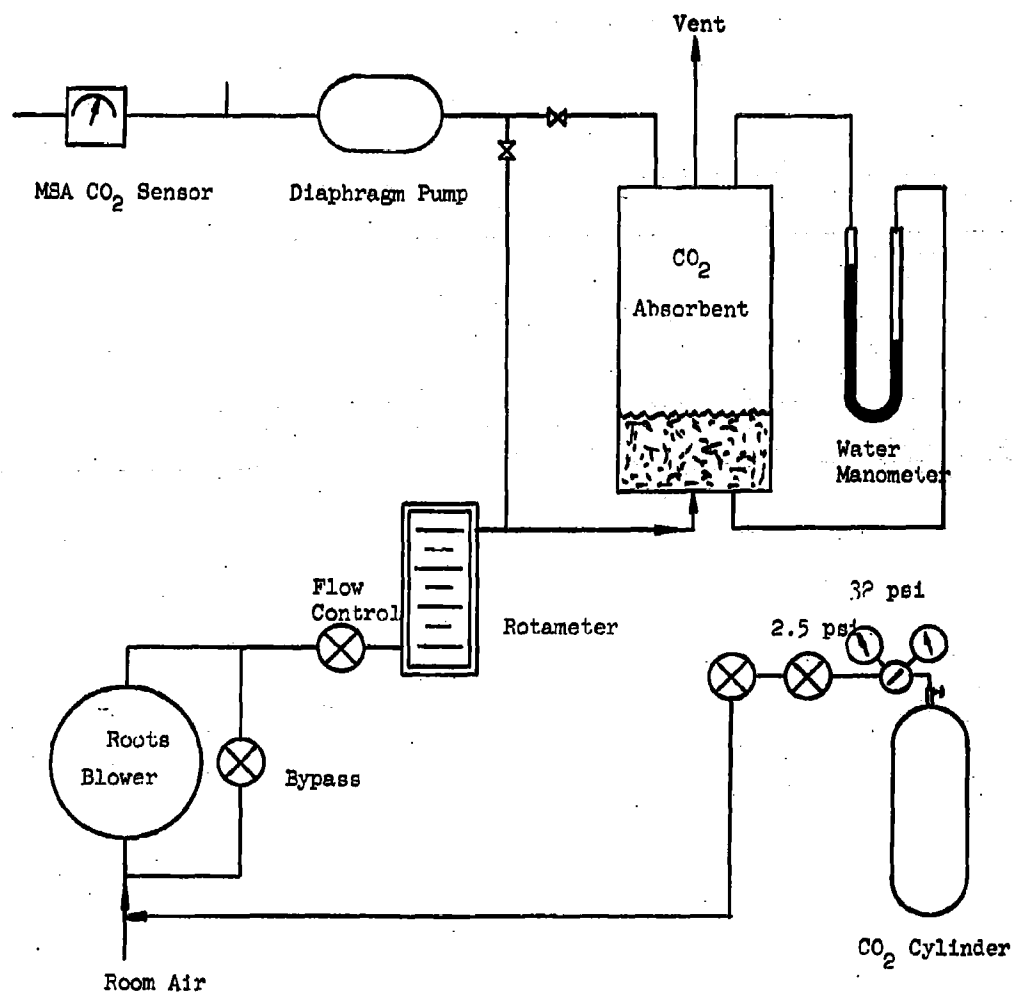
Figure 24   APPARATUS FOR EVALUATING CO$_2$ ABSORBENTS

TABLE 17

SODA-LIME
Experimental and Calculated Data

L,Bed Length, In.	Volume Flow, CFM	Breakthrough Time, Hrs.	Packing Weight, Ib.	Bed Temperature, °C	Lb of CO_2 Absorbed	Lb of CO_2 Lb of Bed	1/V, Sec/Ft
13*	2.5	12.4	9.80	30	2.005	0.210	3.88
13*	6.0	2.63	9.97	30	1.046	0.105	1.62
13	0.323	3.88	0.674	30	0.0831	0.123	2.28
13	0.222	8.50	0.703	30	0.125	0.178	3.32
13	0.563	1.33	0.695	30	0.0496	0.0714	1.31
20	0.210	24.3	1.126	30	0.338	0.301	3.51
20	0.320	12.7	1.129	27	0.272	0.241	2.30
20	0.737	2.45	1.116	30	0.120	0.107	1.00
20	0.355	11.0	1.120	30	0.259	0.231	2.08
20	0.485	5.25	1.116	30	0.169	0.151	1.52
20	0.737	2.28	1.113	30	0.111	0.100	1.00
20	0.337	11.2	1.110	30	0.250	0.225	2.18
26	0.553	6.50	1.423	30	0.238	0.167	1.33
26	0.195	39.2	1.477	30	0.507	0.356	3.78
26	0.31	19.3	1.436	30	0.397	0.276	2.38
26	0.337	14.5	1.460	32	0.319	0.218	2.18
13	0.357	1.70	0.822	30	0.0402	0.0490	2.06
13	0.736	0.40	0.813	30	0.0195	0.0240	1.00
13	0.210	9.66	0.804	30	0.134	0.167	3.51
20	0.362	7.40	1.257	30	0.177	0.141	2.04
20	0.210	25.5	1.242	30	0.355	0.286	3.51
20	0.744	1.36	1.267	30	0.0720	0.0530	0.99
26	0.368	16.6	1.621	30	0.401	0.247	2.0
26	0.736	1.80	1.630	30	0.0878	0.0539	1.00
26	0.200	38.9	1.570	30	0.515	0.328	3.68
39	0.355	30.6	2.340	30	0.720	0.308	2.08

* Tests in six-inch diameter column

In order to correlate the experimental results with the theoretical considerations in Section 3.1.2, the results were plotted for soda-lime in Figures 25, 27, 31 and for Baralyme in Figures 26, 28, and 32. An attempt was made to correlate the reaction velocity constants and the corresponding active site numbers as functions of velocity and length. However, it was found that these variables were very sensitive to experimental deviations and that no correlation could be obtained on this basis. As a result, a more empirical approach using graphical procedures was developed and a satisfactory correlation was obtained.

Figures 25, and 26 show the effect of velocity on the breakthrough time for each of the three lengths tested. The theory predicts that these curves should be straight lines intersecting the reciprocal velocity axis at velocities where the breakthrough time is essentially zero. A comparison of Figures 25 and 26 shows that soda-lime agreed more closely with the theory than Baralyme. The convergence of the times at high velocities indicate that channeling prevails at these conditions and therefore, even with high packing lengths, very little capacity can be expected.

Breakthrough capacity as a function of reciprocal velocity with length as the parameter is shown in Figures 27 and 28 for soda-lime and Baralyme, respectively. As could be expected, breakthrough capacity increases with increasing length and decreasing velocity. The runs made with the six-inch column are designated by two dots above the 13-inch line in Figure 27. The curve crossing horizontally through the 20- and 26-inch curves represents a locus of column dimensions and velocities for which the required absorption performance will actually be realized at 24 hours. The maximum capacity for each substance based on the total reactant available is 0.48 pounds of CO_2 absorbed per pound of absorbant. Therefore, the capacities for each length will asymptotically approach 0.48 on the ordinate axis.

Figure 31 and 32 show the effect of velocity and bed length on the pressure drop for each material in the 1.5-in ID column. The pressure drop for each scaled-up column will be slightly higher than given in Figures 31 and 32 due to wall effects.

3.2 Static Carbon Dioxide Absorption

A static absorption system, which utilizes natural convection currents has the advantage of not requiring a blower for forced circulation and therefore is not dependent upon a power supply, whether manual or electrical.

A satisfactory absorbent should have the following properties:

1. Dust free- to prevent irritation and possible injury to the eyes and respiratory organs

2. Nontoxic- to prevent injury in the event of accidental contact with the material

3. Low required exposed surface area- to conserve space.

Soda - Lime

Effect of Column Length and Superficial Velocity
on the Breakthrough Time

Figure 25

Baralyme
Figure 26

Effect of Bed Length and Superficial
Velocity on the Breakthrough Time
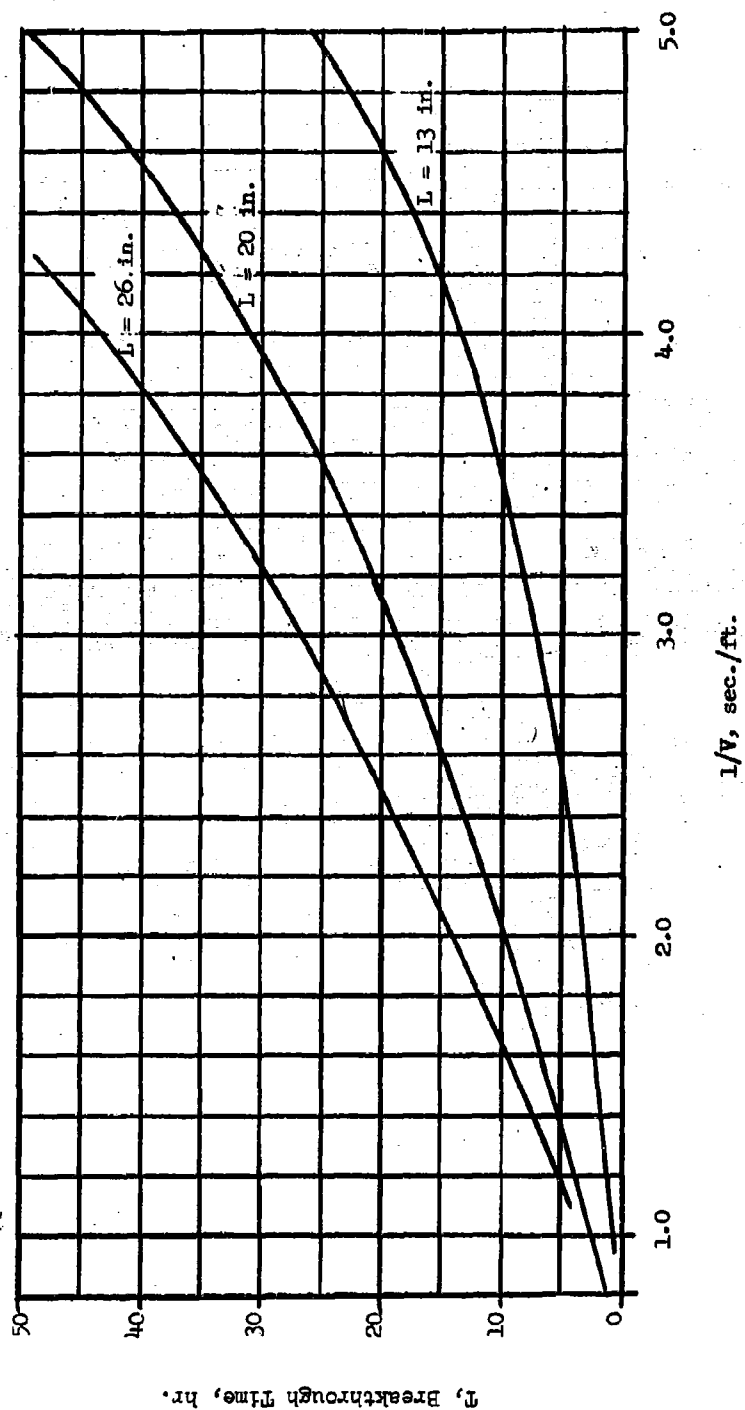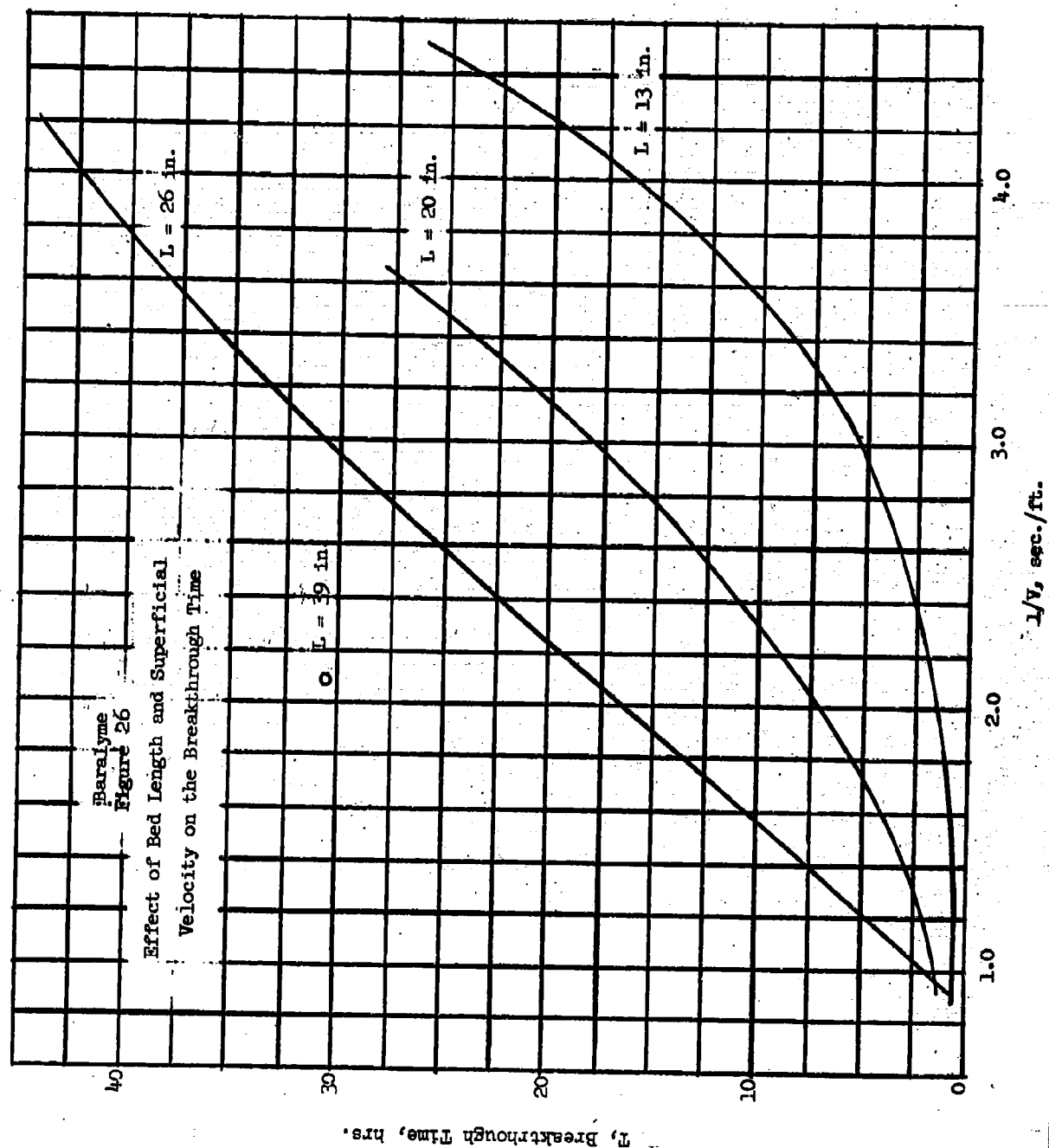
Soda-Lime

Breakthrough Absorption Capacity
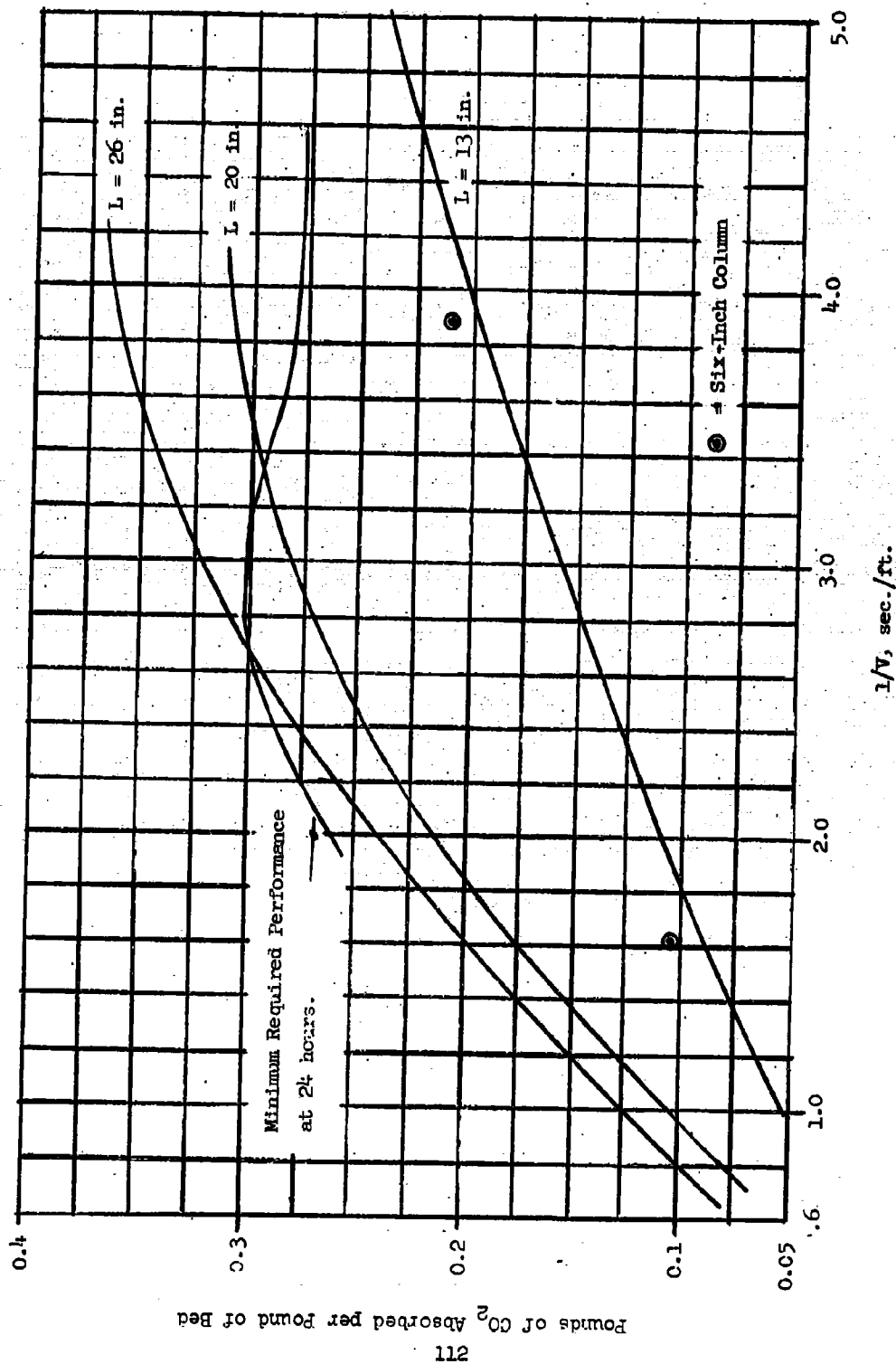
Figure 27
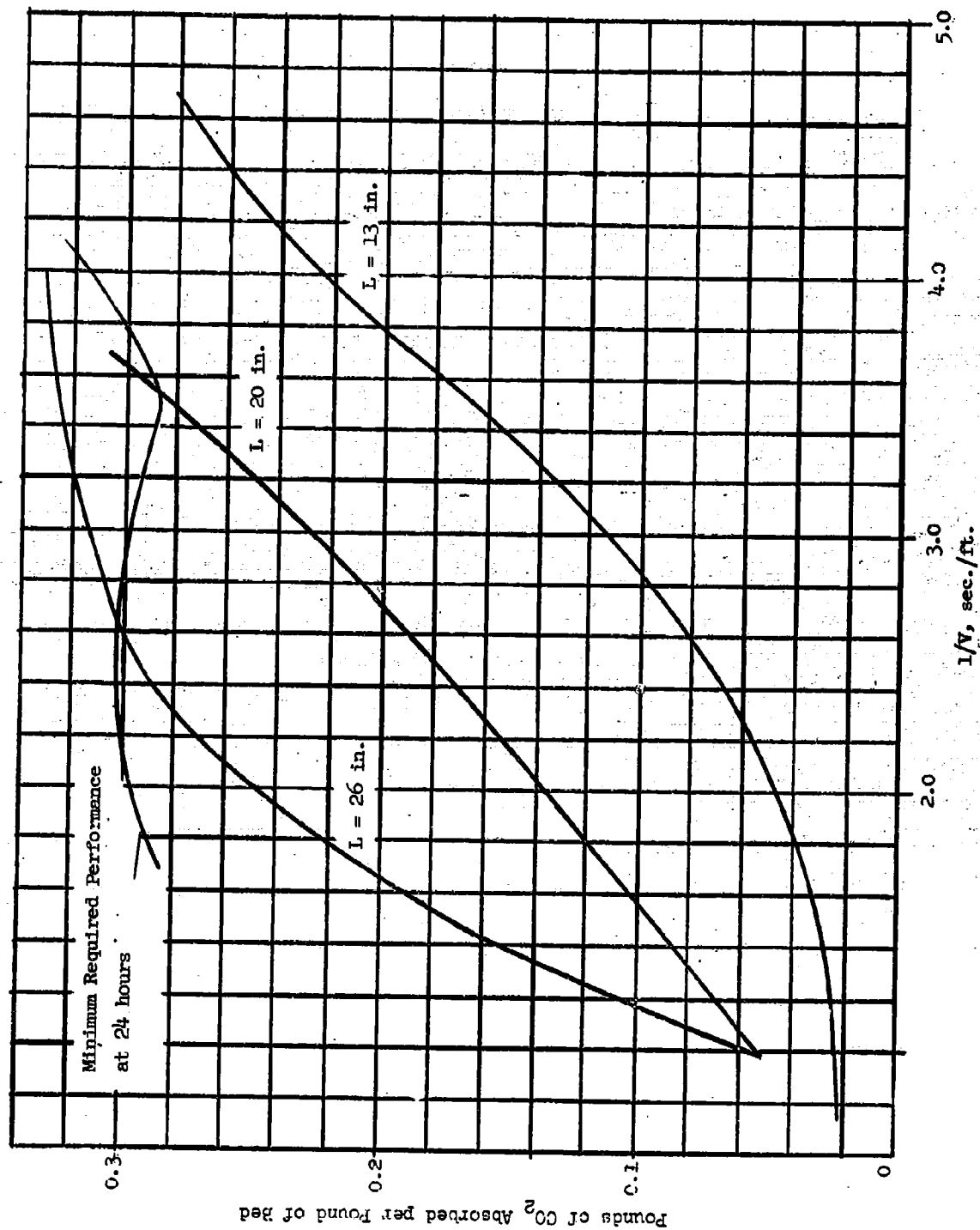
Figure 28 BARALYME BREAKTHROUGH ABSORPTION CAPACITY

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Figure 29 SODA-LIME PERFORMANCE CHARACTERISTICS
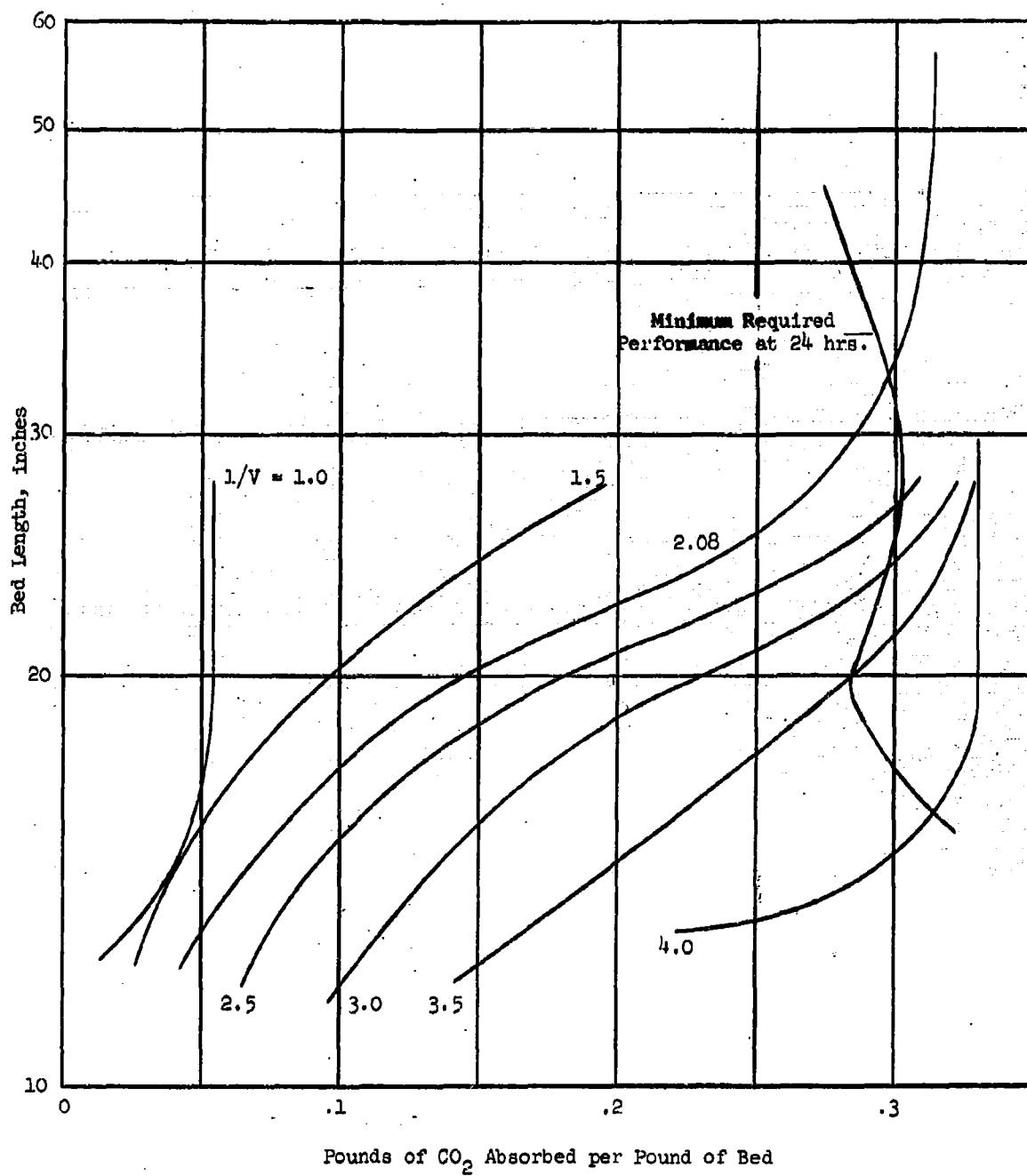
Figure 30   BARALYME PERFORMANCE CHARACTERISTICS

1.5 in. I.D. Column
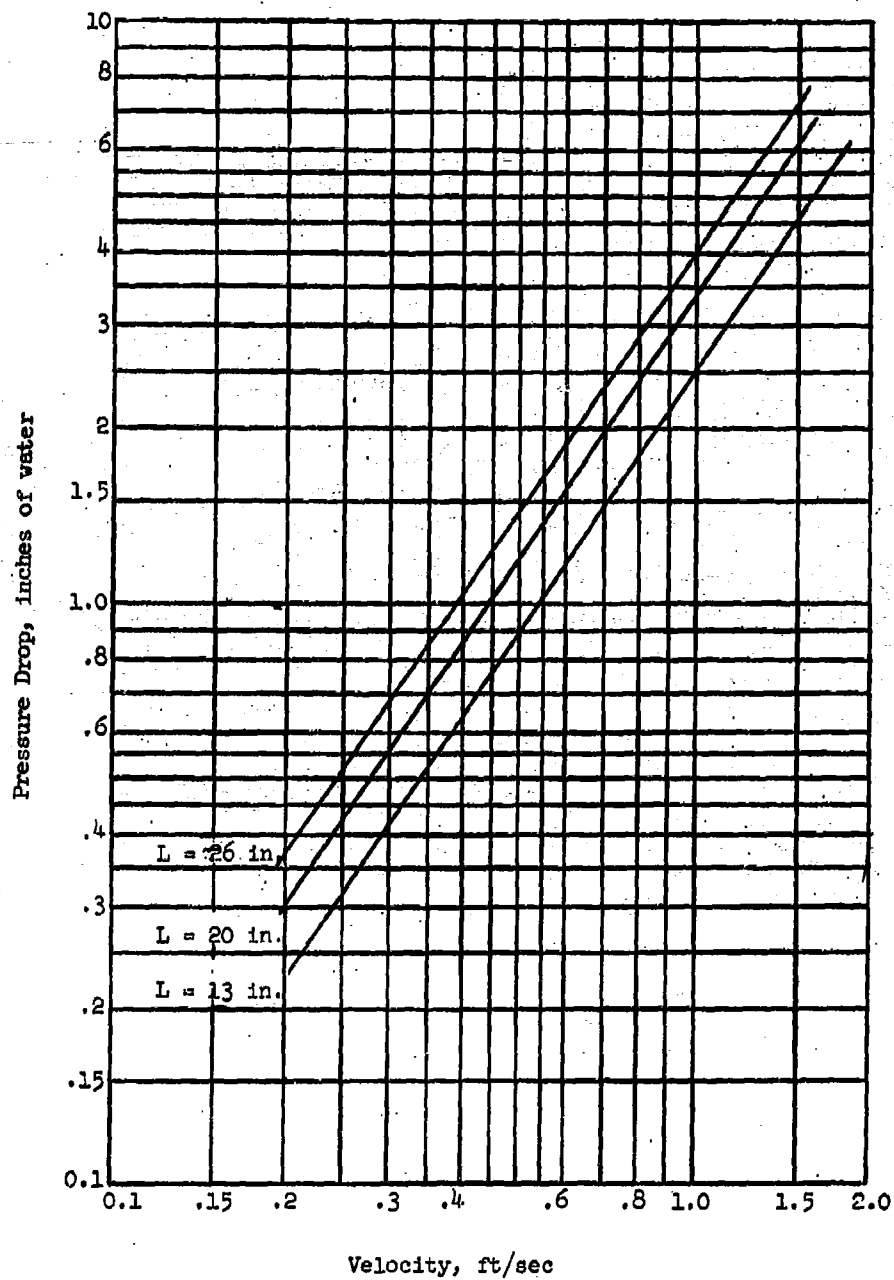
Figure 31 · SODA-LIME
EFFECT OF VELOCITY AND BED LENGTH ON PRESSURE DROP

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1.5 in. I.D. Column

Pressure Drop, inches of water

L = 26 in.
L = 20 in.
L = 13 in.

Velocity, ft./sec.
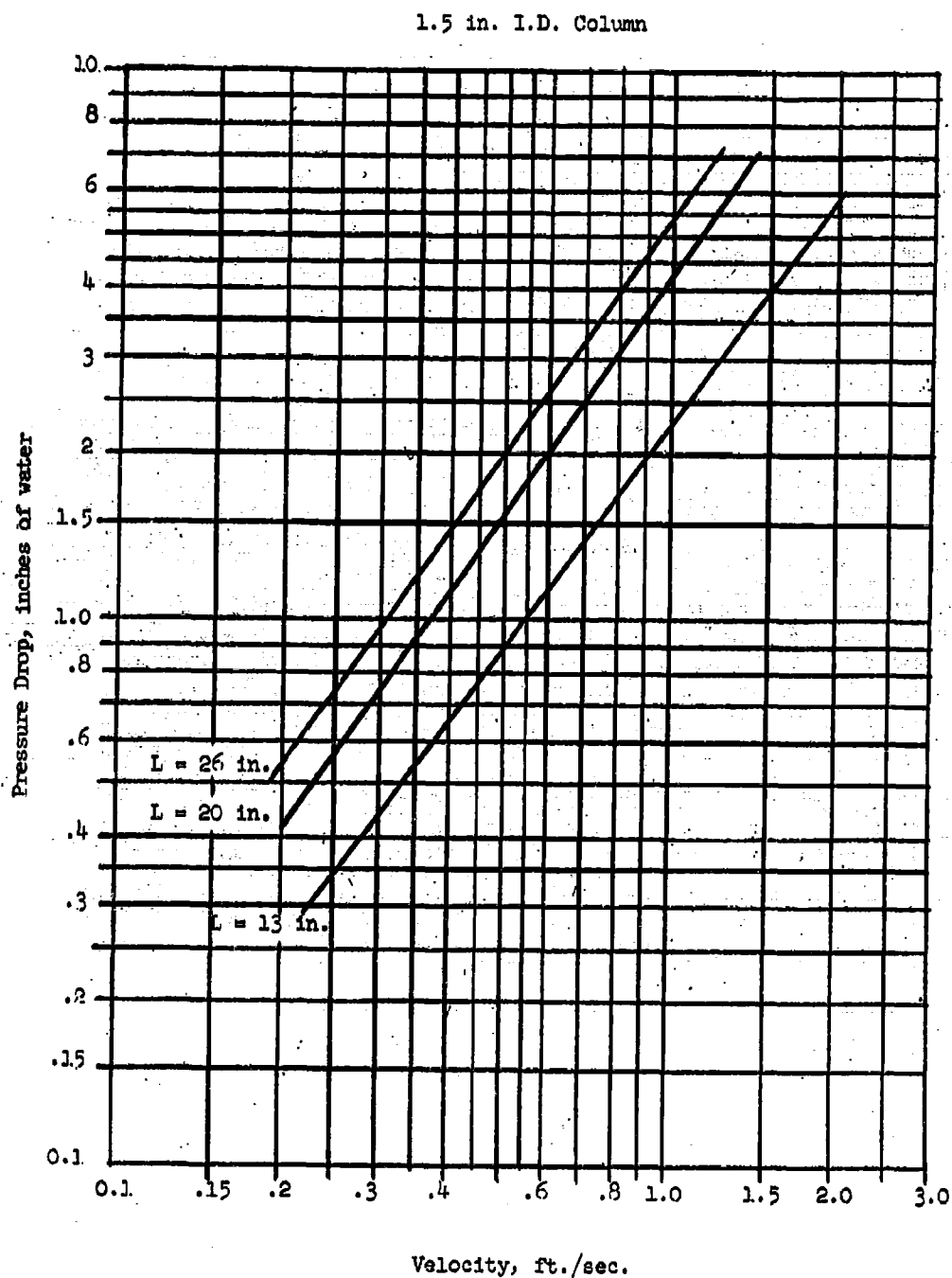
Figure 32 BARALYME
EFFECT OF VELOCITY AND BED LENGTH ON PRESSURE DROP

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3.2.1 Background

Of the various solids which may be satisfactorily used in a blower - canister system, anhydrous lithium hydroxide is the only material available at the present time which is sufficiently active to absorb carbon dioxide in a static system.

At the present time, Maywood Chemical Works is the only lithium hydroxide manufacturer known to be marketing the anhydrous material for fallout shelter use. This material is the 4/8 mesh granular form sold under the tradename of "Granlox". It is sold in four-pound and eight-pound containers. The four-pound container is advertised to be adequate for one person for 48 hours. Maywood Chemical Works' recommendations call for spreading the material on a screen at least 1-1/2 ft x 3 ft so that the air can circulate through the material.

3.2.2 Test Procedures

The diagram below shows the experimental setup that was used to evaluate a static system using anhydrous lithium hydroxide as a carbon dioxide absorbent.
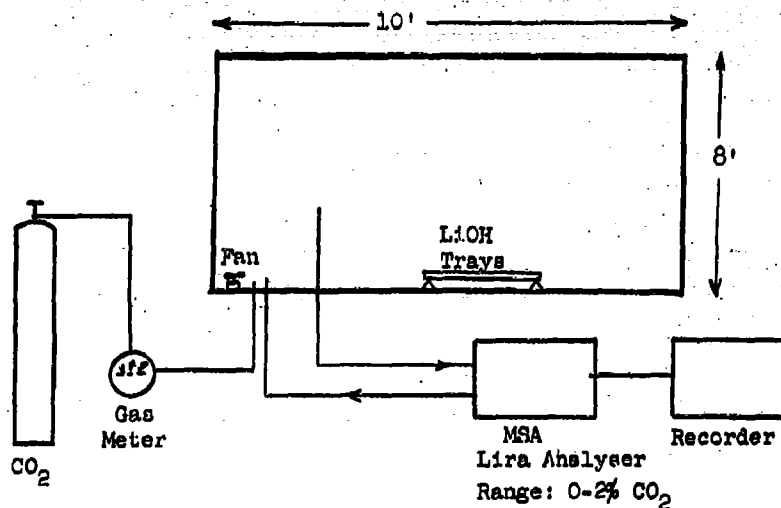
The carbon dioxide was released into the chamber and circulated by means of a 10-cfm fan. The purpose of the fan was to promote circulation which ordinarily would be provided by the movement of the habitants and thermal convection. The fan also insured that a representative air sample would be obtained at the CO_2 sensor. The "Granlox" was spread over two 1-1/2 ft x 1-1/2 ft trays. Since this provided only for contact from a single surface as compared to the double surface of a screen, one could reasonably expect only one-half the absorption rate.

3.2.3 Results

Several runs were made to determine the rate of carbon dioxide absorption per square foot of exposed lithium hydroxide. When carbon dioxide was added to the chamber at a rate of 1.2 cubic feet per hour the concentration increased at a rate of 0.12 per cent per hour. This indicates that the 4.5 square feet of "Granlox" were absorbing CO_2 at a rate of 0.5 cubic feet per hour.

Therefore, to control the carbon dioxide production of one person an exposed surface of 8 to 10 square feet would be required. This value agrees reasonably well to the figure of 4.5 square feet of screen that Maywood Chemical Works recommends because a screen has two exposed surfaces and allows easy passage of the air through the granules.

The problem of dust formation was found to be severe. When the "Granlox" was poured from the container an irritating dust forced the experimenter to leave the chamber. This dust also formed when the poured material was spready evenly over the surface of the tray. This problem is a serious disadvantage for the use of anhydrous lithium hydroxide in a static system.

3.2.4 Conclusion

Anhydrous lithium hydroxide will absorb carbon dioxide in a passive environmental control system, however, the dusting problem places serious limitations on its application.

SECTION 4

APPLICATION STUDY

4.1 Oxygen Supply

The oxygen consumption for a man varies from person to person and for the same person depending upon his state of activity and/or emotional stress. As explained in Section 2.1, the average adult during sedentary activity consumes approximately one cubic foot of oxygen per hour. This value will be used as the basic requirement in designing oxygen supply systems.

4.1.1 Application

A shelter can satisfactorily be supplied with oxygen from either chlorate candles or high pressure gas cylinders. These two methods are nearly equal when safety, reliability and ease of handling are considered. Therefore the deciding factor is cost, although it must be mentioned that high pressure gas cylinders are now commercially available in large quantities whereas a family-size chlorate candle is still in the development stage.

A cost comparison dictates the choice of a chlorate candle for a shelter designed for less than four persons. If the shelter is designed for four or more people, the more desirable method of oxygen supply would be the use of the high pressure gas cylinders. The number and size of cylinders depends upon the design capacity of the shelter.

One commercial 244-cubic foot capacity oxygen cylinder will furnish oxygen for 10 persons for 24 hours, or two of these cylinders will take care of 20 people. If 12 persons are present in the shelter with one 244-cubic foot cylinder the stored oxygen will become depleted in 20-21 hours. Then the oxygen from the room will be used. As shown in the chart below, if 100-cubic foot of shelter volume is available for each person, the oxygen concentration will fall to 16 per cent in the period from 20 hours to 24 hours.

Assume Shelter Volume = 100 ft^3/person

		Stored O_2 Depleted In	Concentration at 24 Hours
(1)	10 Persons/244 ft^3 Oxygen Cylinder	24 hours	20%
(2)	12 Persons/244 ft^3 Oxygen Cylinder	20.3	16
(3)	14 Persons/244 ft^3 Oxygen Cylinder	17.4	13
(4)	16 Persons/244 ft^3 Oxygen Cylinder	15.2	11

TABLE 18   OXYGEN DEPLETION IN A SEALED ENVIRONMENT

In a small shelter the cylinder would best be placed in the horizontal position so as to eliminate the danger of knocking over. In larger shelters provisions can be made to secure the cylinders upright against a wall. If high pressure tubes are used in large shelters, they will have to be mounted in the horizontal position. A concrete stand is recommended for installation of 1500 cu. ft. capacity tubes. The advantage of using high capacity cylinders is that less cylinders are required.

An example of two sizes which could be used for a 100-person shelter is shown below.

Number	Type	Volume
10	244 ft^3 cylinder	2440 ft^3 oxygen
6	400 ft^3 cylinder	2440 ft^3 oxygen

4.1.2 Cost and Space Requirements

For four or less persons the use of chlorate candles is more economical. The Maywood Chemical Works is presently developing a candle advertised to be capable of supplying 48-man-hours of oxygen. This unit is not presently available but when marketed the price is expected to be approximately $10 for the candle and $12 to $15 for the required burner. Thus the total cost of providing oxygen for 48 man-hours by this method is $25. per person. Information as to the present stage of development and probable price when produced in quantity has not been released by the Maywood Chemical Works. The self-contained chlorate candle which liberates 90 cu. ft. of oxygen is manufactured by the MSA Research Corp. at a cost of $60.00. Since the oxygen is released over a period of one hour, a design change would be necessary to release the oxygen over a period of 24 hours. Assuming no major increase in cost for a new design, the cost per person would be $15.00. This is several times as expensive as the use of high pressure cylinders. MSA has given no indication of price reductions for large quantities of these candles.

Table 19 shows the costs and space requirements for installing oxygen supply systems in 10-100- and 1000-man shelters. Although provisions for manifolding would reduce the amount and degree of monitoring and maintenance required, the cost is considered prohibitive. However, a small plastic flowmeter such as the Dwyer No. 490-10 costs only $9 and would prove extremely helpful in adjusting the flow rate of oxygen into the shelter. In shelters where more than one cylinder is installed the regulator-flowmeter assembly must be removed when the cylinder is depleted and attached to another cylinder. A single stage regulator such as the Matheson No. 1-540 costs $31.50. Comparable regulators and flowmeters may be obtained from other manufacturers if desired. The cost of oxygen for small installations i.e., one or two 244 cu. ft. cylinders cost approximately $2.50 per 100 cubic feet whereas in bulk quantities the cost of gas is approximately $1.00 per 100 cubic feet.

TABLE 19

APPLICATION DATA FOR
HIGH PRESSURE OXYGEN STORAGE AND SUPPLY

	Shelter Size (persons)		
	10	100	1000
Total Oxygen Required (cu.ft.)	240	2,400	24,000
Cylinders			
Number	1	6	16
Storage Capacity of each (cu. ft. STP)	244	400	1,500
Dimensions of each	9" x 52"	10-5/8" x 56"	9-5/8" x 20'6"
Total Filled Weight (lbs.)	120	1,164	13,200
Total Floor Space (sq.ft.) (horizontal position)	4	30	506
Total Cost of Cylinders	$38.00	$400.00	$3,584.00
Cost of Regulator and Flowmeter	40.50	40.50	40.50
Cost of Stored Gas	6.00	60.00	600.00
Total Cost	$84.50	$500.50	$4,224.50
Per Person Cost	$ 8.45	$ 5.00	$ 4.23

A similar cost analysis performed in 1959 by the U.S. Naval Radiological Defense Laboratory yielded a per person cost value of only $2.23 (in contrast with $5.00). This source quoted the use of Navy stock cylinders, regulators and gas which may account for the discrepancy. (Ref. 80)

One means of reducing the cost of the oxygen supply is to develop a dependable low cost regulator-flowmeter. It is realized that a needle valve could be substituted for the regulator and reduce the cost from $30 to $10, but needle valves have the disadvantage of requiring frequent regulation and will develop full tank pressure in the event of plugged line or flowmeter.

4.1.3 Power

Neither chlorate candles nor high pressure gas cylinders require any power.

4.1.4 Availability

Oxygen is readily available from such distributors as the Air Reduction Company, Air Products, Inc., Linde Company, Liquid Carbonic Division of the General Dynamics Corp., National Cylinder Gas, Thomas A. Edison Industries - Medical Gas Division, and the Matheson Company.

Various producers of high pressure oxygen cylinders include the Pressed Steel Tank Company, Harrisburg Steel Company, Taylor-Wharton Company, and the Marison Company.

Chlorate candles are produced by the Maywood Chemical Works and Mine Safety Appliance Company. These are not commercial items so very large quantities are not readily available.

4.2 Carbon Dioxide Removal

The static absorption tests utilizing anhydrous lithium hydroxide as described in Section 3.2 showed that this material had such an excessive tendency to dust that its use is not recommended. Lithium hydroxide could be used in blower-canister systems but both soda-lime and Baralyme are less expensive. Therefore, the use of soda-lime or Baralyme flower-canister systems as described below are recommended for carbon dioxide absorption in closed shelters.

4.2.1 Application

Cross-plots of Figures 27 and 28 were constructed in order to facilitate the scale-up design of the bed lengths. These are shown in Figures 29 and 30 for soda-lime and Baralyme respectively. The vertical curve crossing the constant reciprocal velocity curves again represents a locus of column parameters which will absorb the required amount of CO_2 up to 24 hours. The requirement is based on the figure of 0.85 ft^3 of carbon dioxide produced per hour per man. For a 10-man design the total carbon dioxide production is 8.5 ft^3 per hour or at one per cent this represents 850 ft^3 of shelter air per hour which must be treated by the absorbent. In a 24-hour period, the absorbent should remove 22.6 pounds of carbon dioxide up to breakthrough at 0.1 per cent. The actual column sizes which will give the required performance are listed in Table 20.

TABLE 20

SODA-LIME, WORKING DESIGNS

10 Men, 24 Hours

1/V, Sec/ft	Column Length In.	Lb. CO_2 Absorbed per Lb. of Bed	Column Diameter In.	Absorbent Weight Lb.	Estimated Pressure Drop, In. Water
1.87	42.5	0.251	9	90.7	2.5
2.31	30.7	0.282	10	80.9	1.4
2.80	23.7	0.301	11	75.5	0.8
3.32	20.0	0.292	12	75.9	0.6
3.90	18.0	0.285	13	80.1	0.4

BARALYME

1/V, Sec/ft	Column Length In.	Lb. CO_2 Absorbed per Lb. of Bed	Column Diameter In.	Absorbent Weight Lb.	Estimated Pressure Drop, In. Water
1.87	36.0	0.292	9	76.8	3.0
2.31	30.0	0.301	10	79.0	2.1
2.795	25.5	0.298	11	81.3	1.3
3.325	21.6	0.290	12	82.0	0.8
3.90	16.7	0.304	13	74.3	0.4

The possible experimental deviations and various conditions in actual use would probably smooth over the differences between the predicted absorbent weights for each velocity. Since a scale-up method was used to predict the column diameters, the predicted weights (and therefore, lengths) will be slightly lower than necessary in operation. This is due to the fact that end effects will be realized with the smaller length to diameter ratios

of the scaled-up columns. In order to include a safety factor in the design, the column length may be increased to the desired percentage of safety. The effect of increasing the length at a given diameter will be to increase the capacity, the breakthrough time and the pressure drop.

Various column sizes are given in Table 21 in order to emphasize the fact that more than one size will do the required job. The best size depends on the criteria of judgment which include power requirements (pressure drop), columncosts and absorbent costs. The choice of the best column will depend on an optimization of these variables for individual situations.

Soda-lime column sizes for 100-man shelters have been predicted with the same design curves used for the ten-man system. The physical limits for design are given by a maximum linear velocity of one foot per second and the minimum velocity by the minimum length to diameter ratio. At high velocities, soda-lime breaks down physically with the result of channeling, dust problems and low capacity. The column diameter is increased and the length is reduced at lower velocities, the net result being an increased absorption capacity and a substantial saving of material. The apparent optimum for soda-lime is in length to diameter ratio (L/D) of approximately 1.0. However, the experimental data do not show the end effects of a small L/D because the column used here had an L/D much larger than this value. It is expected that actual capacities in small L/D columns will be somewhat less than predicted on the basis of the present experiments. Further experiments on a larger scale would be necessary to determine the L/D below which end effects are important and capacity is effected.

As shown in Table 21, working 24-hour designs have been categorized into one, two and three separate units. A two-unit system consists of two towers in parallel with each having the capacity to treat one-half the flow of a single unit. For a given linear velocity, the advantage of using two or three units in parallel is to reduce the required column diameter. The reason for doing this is to increase the L/D and to bring the column to a practical and readily available size. At the same time, two disadvantages which arise with multiple units are increased column investment and increased power requirement due to extra pipes and fittings.

The apparent best design for soda-lime considering factors mentioned above is a two-tower system in parallel, 20-inch inside diameter and an absorbent length of 44 inches. This requires a volume of 8 cubic feet and 463 pounds of absorbent for each unit (based on 58 lb. per cu. ft. bulk density). Each unit can treat one percent CO_2 in air for 24 hours at a rate of 4250 cu. ft. per hour or 0.541 foot per second superficial linear velocity. Based on a pressure drop over the bed of 3.2 inches of water, the total power required for both units is 0.0715 HP. These specifications do not include a safety factor for scale-up errors or other unknown factors.

TABLE 21

SODA-LIME, WORKING DESIGNS

100 Men, 24 Hours

One Column

Column Diameter, in.	Area, ft^2	1/V, sec/ft	Lb. CO_2 Absorbed per lb of Absorbent	Packing Length, in.	Packing Weight, lb	Estimated Pressure Drop, in. Water
20.8	2.36	1.0	0.167	120	1370	40
25.5	3.54	1.5	0.218	60	1027	9
29.4	4.72	2.0	0.262	38	867	2.5

Two Columns
Specifications of One Unit

14.7	1.18	1.0	0.167	120	685	40
18.0	1.77	1.5	0.218	60	514	9
20.8	2.36	2.0	0.262	38	434	2.5
23.3	2.95	2.5	0.292	27.5	392	1.1

Three Columns
Specifications of One Unit

12.0	0.79	1.0	0.167	120	456	40
14.7	1.18	1.5	0.218	60	342	9
17.0	1.58	2.0	0.262	38	290	2.5
19.0	1.97	2.5	0.292	27.5	262	1.1
20.8	2.36	3.0	0.301	22.3	254	0.6

The same reasoning as applied to soda-lime columns also holds true for Baralyme. Column sizes for 100 men and 24 hours are shown in Table 22. The best design appears to be two columns in parallel, each 20 inches inside diameter, 38 inches of packing and a total volume for each of 6.9 cu. ft. The weight of Baralyme is 400 pounds in each unit, and the pressure drop of 4.5 in. water requires a total of 0.10 HP.

TABLE 22

BARALYME, WORKING DESIGNS

100 Men, 24 Hours

One Column

Column Diameter, in.	Area ft^2	$1/V$, sec/ft	Lb. CO_2 Absorbed per lb of Absorbent	Packing Length, in.	Packing Weight, lb	Estimated Pressure Drop, in. Water
25.5	3.54	1.5	0.270	50	855	10
30.0	4.91	2.08	0.298	33	783	3

Two Columns

Specifications of One Unit

18.0	1.77	1.5	0.270	50	428	10
21.2	2.46	2.08	0.298	33	392	3
23.3	2.95	2.5	0.302	27	385	1.5

Three Columns

Specifications of One Unit

14.7	1.18	1.5	0.270	50	285	10
17.4	1.64	2.08	0.298	33	262	3
19.0	1.97	2.5	0.302	27	257	1.5
20.8	2.36	3.0	0.292	24	274	1.0

In sizing columns for systems larger than 100-man capacity or for longer periods than 24 hours, it would be advisable to use multiple units of the 100-man systems. The reason for this is that columns of larger capacity would involve large weights and cumbersome diameters of 3 feet and above. Thus, a 1000-man system would contain two pairs of columns mentioned above and will require ten times the power.

4.2.2 Cost

The cost of the recommended Carbon Dioxide absorbents is as follows:

Baralyme

In quantities greater than 50 pounds the price of Baralyme is $0.36 per pound. Since 8 pounds are required per person for 24 hours, the man-hour cost is $0.12. The USNRDL study referred to previously quotes a value of $2.10 per man-day or $0.088 per man-hour. (Ref. 81)

Soda-Lime

In drum quantities soda-lime can be purchased for $0.29 per pound. Since 8 pounds are required per person for 24 hours, the man-hour cost is $0.12. The USNRDL study quotes the same value of $2.10 per man-day.

4.2.3 Power

The use of Baralyme or soda-lime requires a blower which is either manually operated or electrically powered if possible. Blowers suitable for this purpose are manufactured by the Roots-Connorsville Blower Division of Dresser Industries, Inc. and the Champion Blower & Forge Company, Inc. In order to maintain the carbon dioxide level at one per cent a circulation rate equal or greater than 100 CFH per person must pass through the absorbent bed.

Assuming a pressure drop of 1.0" H_2O from the blower to the bed outlet and a rate of 100 CFH the theoretical horsepower requirement per person is 2.6×10^{-3} HP.

4.2.4 Volume and Portability

Baralyme and soda-lime have bulk densities of 55 lbs/ft^2 for 4/8 mesh material. Since 8 pounds are required per person, the material volume per person is 0.17 cubic foot. The material should be prepackaged in the columns and sealed so that it will not have to be handled by the shelterees.

4.2.5 Availability

The availability of the three carbon dioxide absorbents recommended, anhydrous lithium hydroxide, Baralyme and soda-lime, are described below. Most chemical firms were hesitant to specify their capacity in producing the chemical of interest. Where this information was available it is mentioned below.

Lithium Hydroxide

The manufacturers of lithium hydroxide include: Foote Mineral Company, Lithium Corporation of America, Var-Lac-Oil Chemical Co., and Maywood Chemical Works. It is believed that most firms produce large amounts of the monohydrate, $LiOH \cdot H_2O$, but only limited amounts of the anhydrous material. As an example Foote Mineral Company can produce 750 tons/month of the monohydrate but at the present time are producing only small amounts of the anhydrous material which passes U.S. Navy specifications MIL-L-202130. Foote Mineral Company will be able to produce large additional amounts of the anhydrous material within a few months.

Maywood Chemical Works is presently marketing four-pound packages of LiOH for family shelter use under the trade name, Granlox.

Baralyme

Baralyme is marketed only by the Medical Gas Division of the Thomas A. Edison Industries. A realistic figure of the present capacity is approximately 20 tons/month. They estimate that their plant capacity could be increased 50 tons per month.

Soda-Lime

The soda-lime producers include the Mallinkrodt Chemical Works and Dewey and Almy Division of W. R. Grace and Company. No data is available on plant capacities but soda-lime is believed to be available in large quantities because it is widely used in hospital breathing apparatus.

4.3 Odor and Contaminant Removal

Traces of toxic substances must be removed from a shelter to prevent injury to the health of the persons within the shelter and obnoxious substances must be removed for the purpose of maintaining comfort. Generally both properties are contributed from the same compound.

Practically all of the contaminants found within a shelter would be removed by activated carbon. The exception is carbon monoxide and a few low molecular weight gases. Acid gases such as hydrogen sulfide will be removed by the carbon dioxide absorber and thus present no special problems.

Special processes are required for the removal of carbon monoxide. These include catalytic oxidation with Hopcalite, palladium deposited on silica gel, a hot platinum wire, or absorption in a solution of a cuprous chloride in hydrochloric acid also accomplishes the absorption.

4.3.1 Application

Activated carbon may be used passively by containing the material in fine mesh bags which can be distributed throughout the shelter or near places where odors originate. In a family shelter this would probably be the only odor control needed. If a simple low cost carbon monoxide eliminator were developed, this would add to the safety of the family shelter.

Shelters designed for 100 persons or more would probably have an air circulation system in which canisters of activated carbon could be connected. Otherwise the absorbent could be used passively as recommended for family shelters.

The larger shelters should also have some means of providing carbon monoxide control. The possible means of accomplishing this would be the development of a satisfactory catalytic combustion unit or chemical absorber.

Manual or Powered Blower — CO_2 Absorber — Activated Carbon Odor Control
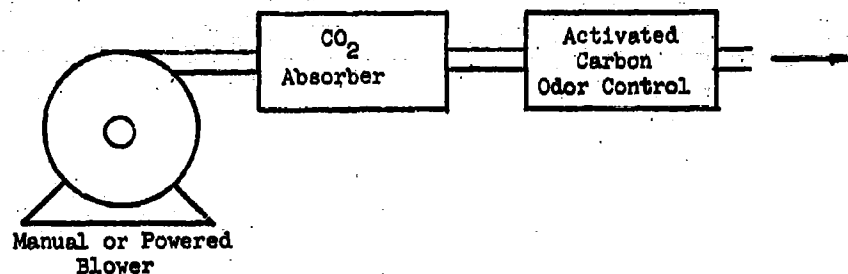
4.3.2 Costs

Assuming that one-half pound of activated carbon was furnished per person at cost of $0.65 per pound, the cost per person would be approximately $0.33. This would vary depending upon the quantity of purchases.

Hopcalite is not sold as such but only in catalytic oxidation units designed and constructed by the Mine Safety Appliance Corporation.

4.3.3 Power

Power is not required for contaminant removal, however, if it is available the adsorbent can be added to a blower-canister system.

4.3.4 Volume and Portability

The volume of activated carbon required is very small. One cubic foot would take care of 70 - 100 persons. Its low density would result in ease of handling.

The size and weight of other units would depend upon their design.

4.3.5 Availability

Activated carbon is readily available from commercial sources. These include Barneby-Cheney Company, Pittsburg Coke and Chemical Company, Allied Chemical Corps, Atlas Chemical Industries, National Carbon Co., Mallinkrodt Chemical Works, Collier Carbon and Chemical Corp., and American Norit Co. Hopcalite is available only through the Mine Safety Appliance Corporation.

4.4 Thermal Control Equipment

As shown in Section 2.4 thermal control equipment may be required in many cases dependent upon the heat gain per unit area of wall surface, initial soil temperature, and the soil thermal properties. For purposes of equipment sizing the estimated dimensions for three classes of shelters and the estimated total heat gain are listed in Table 23. The average heat per person for the family shelters is larger because of the possible use of chlorate candles (recommended for oxygen supply for shelters occupied by less than five persons), and the need for desiccants, which are exothermic, for moisture control.

The method of Reference 70 is again used to estimate the heat loss through the shelter walls so that the thermal equipment may be sized accordingly. The equation is shown below.

$$q = f(F, N) \, \theta_i \, U'/R$$

where, q = soil heat absorption rate, decreasing with time, $Btu/hr\text{-}ft^2$

θ_i = temperature difference, air temperature to be maintained in the shelter minus initial soil temperature, $^\circ F$

U' = coefficient of heat transfer between conditioned space and wall, $Btu/hr\text{-}ft^2\text{-}^\circ F$

R = factor involving the ratio of the volume of heated soil around an equivalent cylinder or sphere to that around the actual configuration

F = value to account for the decreasing heat transfer with time due to the increase in soil temperature

N = value to account for the ratio of the film conductance to the soil conductivity.

TABLE 23

ESTIMATED DATA FOR HEAT LOSS CALCULATIONS
(Construction Material - 3-inch Concrete)

Shelter	Dimensions	Heat Gain	Heat Rate/Unit Area
10-man	10 ft x 12 ft x 8 ft	7,000 Btu/hr	11.8 Btu/hr-ft^2
100-man	30 ft x 40 ft x 8 ft	60,000	17.0
1000-man	100 ft x 120 ft x 8 ft	600,000	21.8

For periods as short as 24 hours the value of the function, $f(F, N)$ (Ref. 70) is so nearly equivalent to unity that it may be neglected for purposes of simplicity. The material of construction in all cases is assumed to be 3-inch concrete which yields a reasonably high U' of 0.6 Btu/hr-ft^2-°F.
An initial soil temperature of 55°F is assumed. Internal air properties to be maintained are 75°F DBT and 65°F WBT (70.4°F ET).

4.4.1 Ten-Man Shelters

Table 23 shows that a heat dissipation rate through the shelter walls of 11.8 Btu/hr-ft^2 is required. The actual heat transfer rate, q, is estimated as below.

$$q = \frac{U'\theta_1}{R} = \frac{0.6 \text{ Btu/hr-ft}^2\text{-°F} \times 20\text{°F}}{.96} \quad \text{(R is obtained from Ref. 70)}$$

$$= 12.5 \text{ Btu/hr-ft}^2$$

This shows that the walls should be able to conduct heat away at a rate sufficient to maintain a dry bulb temperature of 75°F. A desiccant is recommended for control of relative humidity as described in the following sections.

4.4.1.1 Application - The moisture in the shelters can be satisfactorily controlled by using calcium chloride in a static system. This is accomplished by placing the desiccant in sacks above a pan to catch the drippings of hydrate. The equilibrium moisture at fifty per cent relative humidity is 1.8 pounds of water per pound of chloride. Thus, the minimum amount of desiccant required to control five pounds of water is 2.8 pounds. This is an equilibrium condition and can be reached only after a long period of time. Therefore, an excess of calcium chloride is necessary. Four pounds per person is considered to be sufficient.

4.4.1.2 Costs - The cost of calcium chloride varies from $0.08 per pound for a single 80 pound bag to $0.02 per pound in carload quantities. Below is the price per pound for 94-97 per cent calcium chloride from Dow Chemical Company.

No. of 80 lb. bags	Cost per pound
1	$0.0825
2	0.0685
3-4	0.0646
5-6	0.0585
7-12	0.0545
13 and over	0.0388

The cost of a suitable cloth container and dripping cather or pan should be approximately $2.00. An estimation is that one of these units should be furnished for every 40-pound bag.

4.4.1.3 Power - The use of calcium chloride to remove moisture requires no power.

4.4.1.4 Volume and Portability - One 40-pound sack is sufficient for 10 occupants.

4.4.1.5 Availability - Calcium chloride is readily available from a number of chemical companies. These include: Allied Chemical Corp., Dow Chemical Co., Harshaw Chemical Co., Pittsburgh Plate Glass Co., Wyandotte Chemical Corp. and Eagle-Picher Company.

4.4.2 Hundred-Man Shelters

Table 23 shows that a heat transfer rate through the walls of 17 Btu/hr-ft^2 is required for 100-man shelters. The actual heat transfer rate, q, is estimated below.

$$q = \frac{U'\theta_i}{R} = \frac{0.6 \text{ Btu/hr-ft}^2 - {}^\circ F \times 20{}^\circ F}{0.935} \text{ (R is obtained from Ref. 70)}$$

$$= 12.85 \text{ Btu/hr-ft}^2$$

Since the required amount of heat cannot be transferred through the shelter walls some type of refrigeration system is required during the period of closure. This system should be designed to operate over the entire period of occupancy. For long periods of occupancy the transfer of heat through the wall gradually decreases due to the warming of the soil. The total refrigeration capacity should then be based upon the total load, assuming no heat is transferred through the walls. Also to be considered is that the ventilation system will be opened after 24 to 48 hours. The refrigeration capacity for a hundred-man shelter and 3 CFM per person is 4.17 tons based on outside conditions of 95°F DBT and 80°F WBT, and shelter conditions of 85°F DBT and 72°F WBT (78°F ET).

The load was calculated in the following manner:

Occupants

        100 @ 400 Btu/hr-occupant   =   40,000

Lights

        $(0.1 \text{ watt/ft}^2)(1200 \text{ ft}^2)(3.41)$ =   410

Air Load

Sensible: $(3 \text{ CFM/Occupant})(100)(95-85)(1.08)$ = 3,240

Latent: $(3)(100)(131-98)(0.68)$ =   6,740

                              Total = 50,390 Btu/Hr

                                      or

                                  4.17 Tons

        4.4.2.1 Application - A nominal 5-HP self-contained unit as manufactured by Carrier Corp., York Corp., the Trane Co., or equal is suggested for a 100-man shelter. The unit shall have a total dehumidified air supply of 2100 CFM, of which 1800 CFM is return air, and 300 CFM is outside air. Methods of air supply and return are being investigated under Contract OCD-OS-62-134. A 1/2-HP fan motor is required for the above unit. The Carrier Model No. is 50R6 and has the following dimensions:

                          Height - 64 in.

                          Width - 43 in.

                          Depth - 24 in.

If water is available and the condenser tubes are clean, 4 GPM and 7.5 GPM are required for 65°F and 85°F entering water temperatures, respectively at a condensing temperature of 110°F. The water pressure drop through the condenser at 4 GPM and 7.5 GPM is 0.6 psi and 1.8 psi, respectively. If water is not available, other heat sinks should be investigated. Each shelter site will require a study to determine a feasible heat sink. In selecting the heat sink costs should be given consideration.

4.4.2.2 Cost - The Carrier 50R6 distributor cost is approximately $780 for the base unit. Discharge grilles, a return air base, and a heating coil, if desired, would be extra. The cost of the system installed without considering the power source, heating coil, and duct work is estimated to be $1200 or $12 per person.

4.4.2.3 Power Requirements - The power requirements are as follows:

Compressor	-	5 HP or	3.73 KW
Fan Motor	-	1/2 HP or	.37 KW
Pump Motor	-	1/12 HP or	.07 KW
		Total	4.17 KW

With a shelter equipped with a power source, the compressor and pump power requirements of 3.8 KW could be utilized for tempering the outside air during the winter season. An electrical heater based on 300 CFM and 3.8 KW would have a capacity of tempering the outside air 40 degrees Fahrenheit.

4.4.3 Thousand-Man Shelter

As shown in Section 4.4.2.1 the refrigeration load per occupant is 504 Btu/hr. Therefore, the installed capacity for a 1000-man shelter is 504,000 Btu/hr or 42 tons. The total dehumidified air quantity is 20,000 CFM; 3,000 CFM outside air and 17,000 CFM return air. Based on a shelter area of 12,000 square feet as indicated in Table 23, the CFM per sq. ft. is 1.67.

4.4.3.1 Application - A Carrier Model 41EE044 (540,000 Btu/hr Nominal Capacity) with a shell and coil condenser is applicable to shelters which have a water source. The condenser water requirements based on a 110°F condensing temperature, 65°F entering water, and clean tubes, is 34 GPM. For entering water of 85°F the water requirement is 62 GPM. Model 41EG044 is available for application with a remote air cooled condenser or an evaporative condenser. The type of condenser to be used on each shelter must be determined upon surveying each site. The physical size of the unit is as follows:

	Air Discharge	
	Vertical	Horizontal
Width	10'-6-1/2"	10'-6-1/2"
Depth	3'-10-1/2"	6'-4-3/4"
Height	8'-10"	6'-3-3/4"

4.4.3.2 _Costs_ - The cost of the nominal 45-ton self-contained unit with a water-cooled condenser is approximately $6,800. The installed cost per occupant without considering the power source and the ductwork, is from $10 to $12.

4.3.3.3 _Power Requirements_ - The installed power requirements for the mechanical refrigeration unit is as follows:

Compressors	--	40.8 KW
Fan Motor	7-1/2 HP	5.6 KW
Pump Motor	1/4 HP	0.2 KW
	Total	46.6 KW

4.5 Alternate Method

As an alternate to closure of the ventilation system intake, the possibility of supplying outside air from a remote intake has been considered. This intake would have to be positioned in an area relatively devoid of combustible matter so that the air drawn into the shelter would be reasonably cool and free of dangerous combustion gases.

Figure 1 on page 6 shows that at least 3 ft^3/min of fresh air are required per person to insure safe levels of oxygen and carbon dioxide. It is impossible to predict the temperature of this incoming air but it is assumed that some means of cooling the air would be required. If the outside air temperature were 500°F, and the desired inlet temperature were 75°F, then approximately 11.5 tons of cooling would be required for a 100-man shelter.

It has been suggested that the air be drawn through long underground ducts to lower the air temperature by heat rejection to the relatively cool soil. A study of the pertinent literature has shown, however, that excessively long lengths of pipe (on the order of 300 ft for one ton) would be required. (Ref. 83)

Since the outside air is to be used for ventilation, an air cycle refrigeration system is well suited to this application in spite of its slightly higher power requirements as compared to the vapor compression system.

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It must be emphasized that a great danger is inherent in the alternate system; namely, dangerous combustion products may be unknowingly drawn into the shelter via the ventilation duct. As a safeguard to this possibility it is suggested that the incoming air be sucked through a large transparent canister of indicating carbon dioxide absorbent, such as soda-lime or Baralyme. If the absorbent were seen to change color, indicating the presence of carbon dioxide in the outside air, the system would be shut down and the internal environmental control system utilized. In this manner any carbon dioxide present in the ambient gases drawn into the shelter would be absorbed before entering the shelter.

To guarantee that the outside air does not contain dangerous amounts of carbon monoxide, a sensor-alarm to warn the inhabitants is required.

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